Characterization and Implementation of Ground Tire Rubber as Post-Consumer Polymers for Asphalt Concrete

Gaylon L Baumgardner

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Characterization and implementation of ground tire rubber as post-consumer polymers for asphalt concrete

By

Gaylon Lynn Baumgardner

A Dissertation
Submitted to the Faculty of Mississippi State University in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Civil Engineering in the Department of Civil and Environmental Engineering

Mississippi State, Mississippi

December 2015
Characterization and implementation of ground tire rubber as post-consumer polymers for asphalt concrete

By
Gaylon Lynn Baumgardner

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Asphalt binder modification is a common method of improving Hot-mix Asphalt (HMA) performance by enhancing mix properties and reducing or delaying three general HMA distress types: deformation (rutting and shoving), cracking (from repeated loads and low temperatures) and general deterioration (raveling and stripping).

Since the early 1960’s, a common modified asphalt alternative has employed reclaimed rubber as an economical and environmental friendly method of recycling waste tires while improving asphalt physical and mechanical properties. Pavement network deterioration combined with increasing material costs makes polymer modification of asphalt binder desirable, with reclaimed rubber from waste tires being an attractive alternative which addresses performance, economics and environmental issues.

The primary objective of this dissertation is to demonstrate the importance of proper processing of all types of modified bituminous binders, whether they be virgin (e.g. styrene-butadiene-styrene (SBS) or styrene-butadiene rubber (SBR)), post-consumer polymers (e.g. ground tire rubber (GTR)) or a combination (GTR plus SBS). To achieve
this four secondary objectives were identified: 1) characterize GTR using thermo-gravimetric analysis (TGA), 2) improve processing of GTR modified binders, 3) improve testing and specifications of GTR modified binders and 4) evaluate mixes containing GTR modified binders.

A simple efficient instrumental, TGA, method to analyze polymers in binary rubber compounds was developed to quantify the functional polymer content available in GTR. TGA analysis provides a better understanding of the general chemical characteristics of GTR used in modification of asphalt binders for production of asphalt paving mixtures.

Results are presented from efforts to optimize GTR modified binder formulations with respect to how GTR loading, GTR particle size, processing temperature and asphalt cement source affect modified binder properties and ability to meet performance graded binder specifications. These results are the basis to establish recommended processing parameters for formulation and preparation of GTR modified asphalt binders.

GTR modified binders were used in: dense graded asphalt (DGA), stone matrix asphalt (SMA) and open graded friction courses (OGFC) and compared to conventional asphalt cement and styrene-butadiene-styrene (SBS) modified asphalt binders. Mixture performance evaluation with respect to binder effectiveness as it relates to the three general HMA distress types.

Keywords: Ground Tire Rubber, GTR, Modified Asphalt, Asphalt Rubber, Terminal Blend, Belt Add Modifier.
DEDICATION

I would like to dedicate this research to my wife Jill, without whose tireless support and understanding of late hours and periods of seclusion this degree would not have been completed. I also dedicate this to my daughter, Dr. January N. Schultz and grandchildren: Weston, Ava and Ella Hazel. May your Mother and I be a guiding example to you of what you can achieve, always believe it can be done and never give up!

IN MEMORIUM

Justin Dwayne (SHOX) Shotts

3 December 1985 – 14 August 2006

I give thanks to God, through my Lord and Savior Jesus Christ, for the knowledge and abilities, He has blessed me with, which made it possible to complete this venture. Through Him, all things are possible!
ACKNOWLEDGEMENTS

The author expresses sincere gratitude to the many people without whose selfless assistance this dissertation could not have materialized. First and foremost, sincere thanks are due to Dr. Isaac L. Howard, my advisor and committee chairman, and to my committee: Dr. E. Ray Brown, Dr. L. Allen Cooley Jr. and Dr. Dennis D. Truax.

Thank you to my employer, Ergon, Inc. as this research is a culmination of primarily non-externally funded work performed and supported by Ergon at the laboratory facilities of Paragon Technical Services, Inc. (PTSi).

Thank you to the staff of PTSi and Mathy Technology and Engineering, Inc. (MTE) for assistance with specimen preparation and testing: Dr. Codrin Daranga, Stacy Glidden, Andrew Gullotte, Mike Hemsley, Trey Jordan, Andy Menapace, Felicia Reid, Gerald Reinke, Sonia Serna and Scott Vehglan. Special thanks to Dr. John Hardee, Dr. Ian Negulescu, Cliff St John and Elton Williams for their contribution to the instrumental testing efforts of ground tire rubber. A very special thanks to Dr. John D’Angelo a great friend and colleague for his support and help guiding the specifications efforts, and for being a good example of what can be accomplished in our years of maturity.

Lastly I would like to thank Dr. Jean-Yves (JYM) Meynard for introducing me to the wonderful world of asphalt. Your patience and tutoring in my early days set the course for a wonderful career.
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<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>A</td>
<td>Asphaltenes</td>
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<tr>
<td>AAPT</td>
<td>Association of Asphalt Paving Technologists</td>
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<tr>
<td>AASHTO</td>
<td>American Association of State Highway Transportation Officials</td>
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<tr>
<td>ABU</td>
<td>Asphalt Blowing Unit or Air Blowing Unit</td>
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<td>AC</td>
<td>Asphalt Cement</td>
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<td>AKDOT</td>
<td>Alaska Department of Transportation</td>
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<td>AMPT</td>
<td>Asphalt Mixture Performance Tester</td>
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<td>Aged Residue</td>
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<td>ARHMG</td>
<td>Asphalt-Rubber Hot Mix Gap-Graded</td>
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<td>Asphalt Rubber Open Graded Friction Course</td>
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<td>ASTM International</td>
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<td>BAM</td>
<td>Belt Add Modifier</td>
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<td>BBR</td>
<td>Bending Beam Rheometer</td>
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<td>BR</td>
<td>Polybutadiene Rubber</td>
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<td>BURA</td>
<td>Built-Up Roofing Asphalt</td>
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<td>C</td>
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<tr>
<td>CAC-DG</td>
<td>Conventional Dense Graded Mixture</td>
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<td>CC</td>
<td>Concentric Cylinder</td>
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<td>Cohesive Energy Density</td>
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<td>dmm</td>
<td>Tenths of Millimeters</td>
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<td>DSR</td>
<td>Dynamic Shear Rheometer</td>
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<td>DTG</td>
<td>Derivative of Thermal Degradation</td>
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<tr>
<td>dyne-s/cm²</td>
<td>Dyne Second per Centimeter Squared</td>
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<td>E*</td>
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<td>HDPE</td>
<td>High Density Polyethylene</td>
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<td>Hamburg Wheel Tracking Device</td>
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<td>HMA</td>
<td>Hot-Mix Asphalt</td>
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<tr>
<td>ISTEIA</td>
<td>Intermodal Surface Transportation Efficiency Act</td>
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<td>LO</td>
<td>Lion Oil Company</td>
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<td>MSCR</td>
<td>Multiple Stress Creep and Recovery</td>
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<td>m-T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>m-Value Critical Temperature</td>
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<td>NCHRP</td>
<td>National Cooperative Highway Research Program</td>
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<td>NR</td>
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<td>OGFC</td>
<td>Open Grade Friction Course</td>
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<td>PAD</td>
<td>Petroleum Administration for Defense</td>
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<td>Petroleum Administration for Defense Districts</td>
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<td>PAV</td>
<td>Pressure Aging Vessel</td>
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<td>Petroleum Administration of War</td>
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<tr>
<td>PB</td>
<td>Polybutadiene</td>
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<tr>
<td>P/F</td>
<td>Pass/Fail</td>
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<tr>
<td>PG</td>
<td>Performance Grade</td>
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PHR  Parts Per Hundred
PKN  Polski Koncern Naftowy Orlen
PMA  Polymer Modified Asphalt
PP   Parallel-Plate
PPA  Polyphosphoric Acid
PS   Polystyrene
Psh  Maltene Solubility Parameter
P-Tc  PAV Stiffness Critical Temperature
PTSi  Paragon Technical Services, Inc.
PVC  Polyvinyl Chloride
R    Resins
RC   Repeated Creep
REOB Refined Engine Oil Bottoms
RMA  Rubber Modified Asphalt
RPA  Rubber Pavements Association
RTFO Rolling Thin-film Oven Test
RUMAC Rubber Modified HMA
S    Saturates
SAM  Stress Absorbing Membrane
SAMI Stress Absorbing Membrane Interlayer
SB   Styrene-Butadiene Block Copolymer
SBR  Styrene Butadiene Rubber
SBS  Styrene-Butadiene-Styrene Block Copolymer
SHRP  Strategic Highway Research Program
SJR   San Joaquin Refining
SMA   Stone Matrix Asphalt
SO    Shell Oil Company
SR    Smithers Rapra
s-Tc  s-Value Critical Temperature
TB    Total Brenstar
TB    Torsion Bar
TCE   Trichloroethylene
TFF   Tertiary Flow Failure
Tfrass Frass Brittleness Temperature
Tg    Glass Transition Temperature
TG    Thermogram or Thermal Degradation Curve
TGA   Thermo-gravimetric Analysis
Tm    Melting Temperature
TOR   Trans Polyoctenamer Rubber
TPE   Thermoplastic Elastomer
TTI   Texas Transportation Institute
TXOT  Texas Overlay Test
UTI   Useful Temperature Interval
VAC   Volume of Asphalt Cement
VADOT Virginia Department of Transportation
VMA   Voids in Mineral Aggregate
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTM</td>
<td>Total Mixture Voids (Air Voids)</td>
</tr>
<tr>
<td>WIDOT</td>
<td>Wisconsin Department of Transportation</td>
</tr>
<tr>
<td>WMA</td>
<td>Warm-Mix Asphalt</td>
</tr>
<tr>
<td>WTI</td>
<td>West Texas Intermediate</td>
</tr>
<tr>
<td>WWII</td>
<td>World War II</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 Background

Asphalt binder modification is a common method of improving Hot-mix Asphalt HMA performance by enhancing mix properties and reducing or delaying three general HMA distress types: deformation (rutting and shoving), cracking (from repeated loads and low temperatures) and general deterioration (raveling and stripping) (Terrel 1989). Four general methods of modification are commonly practiced: addition of special fillers or extending agents (fibers, activated clay, hydrated lime), air blowing or air rectification (molecular restructuring through treatment with air at high temperatures), chemical modification (phosphorous pentoxide, polyphosphoric acid, maleic anhydride) and addition of polymers (natural and synthetic polymers). Most often such additives are introduced directly into the asphalt binder, e.g. polymers which are the most common form of binder modification; however, addition may be to the mixture at the same time as the aggregates.

Paving technologists are continually seeking new ways to design and build longer lasting pavements and have attempted to improve asphalt pavements by adding polymers to asphalt binders for about as long as pavements have been built with asphalt. In fact, the United States Patent Office granted: Letters of Patent No. 142,601 “Improvements in
Compositions for Pavements” in September 9, 1873, Samuel Whiting (Whiting 1873). This patent describes use of 1% Balata Gum, the natural polymeric latex secretion from the Balata plant, in combination with Trinidad Lake asphalt, oils, rosin and various mineral materials to form a composition suitable for paving applications. There seems to be no further documentation of use of this specific composition in actual pavement construction, however, this may be the earliest officially documented use of polymers to modify paving asphalt.

While no roads were documented to use the Whiting (1873) technology, there are undocumented reports of road construction in France utilizing natural rubber (NR) modified asphalts as early as 1902. Since then, about as many polymers have been tried in asphalt as there are reasons for trying them. Today, modification of asphalt binder is a common practice to improve its physical properties and subsequent HMA performance. Modification decreases temperature susceptibility enabling HMA to withstand additional loading and more severe environments (Bahia 1995). Primarily styrene-butadiene polymers (Styrene-Butadiene Rubber (SBR) and Styrene-Butadiene block copolymers (SB) and Styrene-Butadiene-Styrene block copolymers (SBS)) have been used to modify asphalt to improve pavements in Europe and the United States for more than 40 years. It is estimated that styrene-butadiene polymers account for over 65% of the polymers used in asphalt for paving in Europe and over 90% of the polymers used in asphalt in the United States. Use of synthetic polymers, such as SBS, is limited by cost and commercial availability, with recent shortages in supply and increased costs of both synthetic polymers and asphalt prompting use of alternative modifiers.
Since the early 1960’s, a common modified asphalt alternative has employed reclaimed rubber as an economical and environmental friendly method of recycling waste tires while improving asphalt physical and mechanical properties (Heitzman 1992, Bahia 1994, Billiter 1997). Passenger cars and trucks on U.S. highways wear out millions of tires each year (EPA 2012) making disposal of used tires a major environmental challenge. Ground tire rubber (GTR) is a modifier for asphalt binders used in production of hot-mix asphalt (HMA) or warm-mix asphalt (WMA). In fact, asphalt modification currently represents around 2% of the scrap tire market, consuming an estimated 68,000 tons, or approximately 4.2 million tires (EPQ 2012).

Potential benefits of using GTR modified asphalt binders, in addition to disposal of waste tires, are: longer lasting roads, reduced road maintenance, and improved life-cycle costs. In addition, observations have been made that asphalt pavements constructed with open graded mixtures produced from GTR modified asphalt binders have reduced road noise as compared to dense graded asphalt mixtures and portland cement concrete pavements (Hanson et al., 2004, Rasmussen et al., 2008).

Note that tires for different vehicle types have different compositions. For purposes of this dissertation, light trucks and passenger vehicles are referred to as “cars,” while heavy transport vehicles are referred to as “trucks.” For example, Federal Highway Administration (FHWA) class 1, 2 and 3 vehicles (motorcycles, passenger cars and two-axle four-tire trucks) are considered to use car tires and FHWA classes 4 through 13 (buses and all vehicles up to and including seven or more axle multi trailer trucks) utilize truck tires.
1.2 Objectives

The primary objective of this dissertation is to demonstrate the importance of proper processing of all types of modified bituminous binders, whether they be virgin (e.g. SBS or SBR), post-consumer polymers (e.g. GTR) or a combination (GTR plus SBS). To accomplish the primary objective, four secondary objectives were defined. These were:

1. Characterize GTR using thermo-gravimetric analysis (TGA)
2. Improve Processing of GTR Modified Binders
3. Improve Testing and Specifications of GTR Modified Binders
4. Evaluate Mixes Containing GTR Modified Binders

1.3 Scope

This dissertation focuses on bituminous binders used in three primary applications: dense graded asphalt (DGA), stone matrix asphalt (SMA) and open graded friction courses (OGFC). GTR modified binders may also be used in preventive maintenance applications utilizing asphalt emulsions, however, the scope of this document does not include asphalt emulsions. Applications of the findings reported may be extended to asphalt emulsions as a topic of further study. To accommodate industry needs, consideration is given to specific needs of rubber producers, binder suppliers, contractors and agencies. The scope of this effort considers the current state of practice related to GTR modification presented in the following section, and also considers the research needs presented in section 1.5.
1.4 Common Methods of GTR Modification

GTR is produced from whole scrap tires through mechanical shearing and grinding resulting in size-reduced rubber or crumb tire rubber. In the crumb tire rubber market there are two classes of particle size: “ground” rubber (referred to herein as GTR) which is 2.0 mm (10 mesh) and smaller and “coarse” rubber which is larger than 2.0 mm (10 mesh), with a maximum size of 12.75 mm (0.5 inch). Typical sizes of size-reduced rubber used in modified asphalt binders for road construction ranges from about 1.5 mm (1500µm) down to 420µm (15 mesh to 40 mesh) with limited use sizes as small as 177µm and 125µm (80 mesh and 120 mesh). However, finer sized GTR is not as popular or as common as it generally costs more due to additional grinding required to achieve uniform small particles.

There are two primary methods of incorporating GTR into HMA that are generally referred to as the “wet” and the “dry” processes. The wet process blends GTR with asphalt and allows a prescribed reaction time prior to mixing the GTR modified binder with aggregate. The dry process adds GTR directly to the HMA mixture during production, usually added directly to the aggregate prior to introducing the required asphalt binder. Growth in use of GTR modified asphalt pavements can be credited to successful construction of high performance asphalt pavements primarily using GTR modified asphalt binders produced via two versions of the “wet” process: “asphalt rubber,” (AR) commonly referred to as the “wet process” and “rubber modified asphalt” (RMA) also referred to as “terminal blend.”

AR production in the wet process is also known as the McDonald process and consists of blending GTR of a typical maximum size around 1.5 mm (15 mesh) with
asphalt binder at temperatures ranging from 175 to 190°C (≈ 350 to 375°F) and allowing them to react for 30 to 60 minutes before introduction into the hot-mix mixture production process (McDonald 1975, McDonald 1978, Heitzman 1992, Chehovits 1993). This process is normally performed entirely at the HMA production plant using portable rubber mixing facilities. RMA or terminally blended GTR modified asphalt is produced in a similar manner to AR, except that production occurs in fixed blending facilities. RMA generally consists of blending GTR of a size range from 600µm to 177µm (30 to 80 mesh) with asphalt binder at temperatures ranging from 175 to 190°C (≈ 350 to 375°F) and allowing them to react for 60 (+) minutes prior to transfer to large storage tanks. Once mixed, the RMA is stored at elevated temperatures awaiting delivery to hot-mix production facilities in the same manner as conventional asphalt binders. Note that 600µm to 420µm (30 to 40 mesh) are more typical sizes for GTR in RMA, which is commonly referred to as 30 minus rubber.

The original dry process, known as PlusRide™, used reduced sized rubber of the “coarse” variety with a maximum particle size of 6.3 mm (3 mesh) and approximately 65% (by weight) larger than 2.0 mm (10 mesh) intended to replace a portion of the aggregate with coarse rubber particles to achieve a “flexible aggregate” effect. Though dry addition of GTR has had only limited past success, recent efforts have been employed to recycle GTR by dry addition in the hot-mix asphalt mixing process using additives and processing aids (Hines, 2007, Clark, 2014). These recent efforts, known as Asphalt Plus™, generally consist of adding 600 to 420µm (30 to 40 mesh) GTR, along with select additives, to mixtures in a similar manner as PlusRide™ with exception of utilization of considerably smaller rubber particles with the intention of binder
modification in lieu of aggregate replacement. These additives are represented to provide an improved modified asphalt paving binder by incorporating a small amount of additive or processing aid into GTR modified asphalt binder which in turn leads to easier mixing, reduced tackiness, reduced cracking, less permanent deformation, lower life-cycle cost, and longer service life (Burns, 1999).

As with similar dry processes from the late 1980s which incorporated finer rubber particles to partially modify the asphalt binder (Takallou 1987, Takallou 1988, Heitzman 1992), there is concern as to the function of the finer GTR particles. Do they actually react with the binder in the dry process as in the wet process or do they only partially react with the binder; or do they not react with the binder at all, rather acting as inert filler. Conventional mixture blending temperatures and times may be inadequate to achieve the binder reaction necessary in thin films since wet processes occur at much higher blending temperatures. There are many variables associated with performance of GTR modified asphalt binders for production of hot-mix asphalt other than the process or technology used.

### 1.5 Research Needs

Several aspects of GTR modification of asphalt binders are not yet well understood, which leads to a number of unanswered questions with respect to the stated objectives. These questions are posed in bullet form, italic text, at the beginning of each of the sub-sections that follow. These questions lead to and can be addressed by one of four specific research needs directly aligned with the four secondary objectives discussed in section 1.2:
1.5.1 Characterization of GTR.

- How does the rubber composition and content of functional polymer providing modification of asphalt binders determine the degree of modification?

GTR is produced from scrap tire rubber, which is composed primarily of natural and synthetic rubbers as well as carbon black. Natural rubber content generally varies according to tire type. Truck tires have higher natural rubber content than car tires. With new tire technology and increasing costs of synthetic rubber the gap in natural rubber content between truck and car tire formulations has decreased in recent years. It is hypothesized that total hydrocarbon rubber content and the ratio of natural to synthetic rubber are primary factors determining the effect of GTR modification on asphalt binders. Some state departments of transportation (DOTs) actually specify chemical requirements for GTR composition. While chemical requirements are sometimes specified, verification is not typically performed due to the involved nature of the required testing. Therefore, a simple, efficient instrumental method for analysis of composition of GTR used in modification of asphalt binders to be used in construction of asphalt paving mixtures would be beneficial.

1.5.2 Processing of GTR Modified Binders.

- How does the amount, and gradation of GTR needed to provide proper modification, as well as proper processing parameters needed to provide proper interaction of GTR and asphalt, influence on binder properties?

- What is the appropriate amount of time GTR should remain in contact with asphalt binder, and what temperature(s) is important to adequate blending?
• What are the effects of different binder sources with respect to compatibility with GTR and the degree of reaction that occurs?

• Are additives actually interacting with the GTR modified binder or do they serve an altogether different purpose?

Physical parameters such as the amount and gradation of GTR influence how well binder is modified with GTR as well as how the GTR modified binder performs in mixtures. Processing parameters including blending duration and temperature are key to adequate incorporation of GTR into asphalt binder. Asphalt binder source and compatibility with GTR are also important in determining the efficiency of asphalt binder modification. Additionally, the effects of processing aids and additives are not clear. Therefore, a study of the effects of GTR particle size, GTR loading and processing temperatures and duration is warranted in addition to analysis of the effect of asphalt binder source and additives on binder performance.

1.5.3 Testing and Specifications of GTR Modified Binders.

• Do adequate test protocol and purchase specifications exist to provide consistency from GTR modified binders?

Historically, quantification of the performance characteristics of GTR modified asphalt binders was limited to measuring the increase in viscosity of the GTR modified asphalt binder using crude vane viscometers. Introduction of the Superpave® binder grading system introduced far more appropriate tools for asphalt binder testing to measure performance characteristics. However, due to testing geometry limitations, specifically confounding of results due to particle interference in parallel plate testing,
GTR modified asphalt binders generally have not been able to be tested using the Superpave® binder high temperature tests.

In some cases this inability to fully test the material has limited use and adoption of GTR modified asphalt binders. There are existing geometries well known in the rheology field, specifically concentric cylinder (CC) geometries or “cup and bob” geometries, which can handle larger particle sizes typically used as GTR asphalt binder modifiers. These geometries are not well known in the asphalt industry and should be investigated as to their ability to test neat, polymer modified and GTR modified asphalt binders. Additionally, recommendations are needed as to appropriate purchase and acceptance specifications for GTR modified asphalt binders.

1.5.4 Evaluation of Mixes Containing GTR Modified Binders.

- How does the mode of incorporation of GTR into asphalt binders and mixtures change mixture performance properties?

There is concern that “dry” addition of GTR into HMA or WMA mixtures containing binders from varied sources may lack the necessary GTR loading to provide the equivalent binder performance required. Additionally, lack of processing due to limited blending time and temperature in the HMA or WMA process may not provide adequate processing to fully incorporate GTR into the asphalt binder. Inadequately reacted GTR and binder may fail to provide expected performance achieved by binder modified with either terminally blended GTR or binders modified with synthetic polymers such as SBS. Mixture evaluations with respect to mechanical properties, as
well as the effects of moisture, are needed to fully understand how GTR performs in asphalt mixtures in both wet and dry addition methods.
CHAPTER 2
LITERATURE AND PRACTICE REVIEW

2.1 Overview of Literature Review

The scope of this review covers GTR as a post-consumer polymer for use as a modifier in asphalt binders and mixtures and is intended to provide the reader an adequate background of GTR technology so as to understand this research effort and its significance to the technology. Emphasis is placed on the effects of GTR as a binder modifier and, ultimately, mix properties. The information summarized in this chapter is divided into eight sections: compounding and production of pneumatic tires, post-consumer waste products and processes, a comparison of post-consumer to synthetic polymers, post-consumer uses of ground tire rubber, modification of asphalt binders, properties of ground tire rubber modified binders, properties and specifications of modified asphalt binders and asphalt mixture performance.

2.2 Compounding and Production of Pneumatic Tires

Tires are considerably more than black donuts made of rubber used on vehicles to allow transport of people and goods from point A to point B. Waddell defines a tire as a toroidal, high performance polymeric composite which exhibits characteristics of a flexible membrane pressure container providing load carrying capability, cushioning, and
road handling abilities. It encircles the rim of a wheel to absorb and control forces between the axle and the road in a transient environment and thus transmits driving and braking torque, transmits cornering forces, and performs all functions essential to locomotion (Waddell et.al. 1990).

The pneumatic tire, developed in the early 20th century to meet the demands of improved vehicular speed and comfort, is a complex system of interacting rubbery components, each with specific properties for maximum effectiveness. Performance of a tire depends on the component properties, the interaction of these components and the service conditions of the tire. While rubber is the key material, actually, a tire is quite complex and is made of a lot more than rubber. Fibers, textiles and steel are just some of the additional materials that go into tire components such as the inner-liner, body plies, bead assembly, belts, sidewalls, and tread.

Typical materials used to manufacture tires may include but are not limited to:

- Synthetic Rubber
  - Styrene Butadiene Rubber (SBR)
  - Isoprene
  - Butadiene (PB)
  - Butyl Rubber (BR)
  - Halogenated Butyl Rubber
  - Ethylene Propylene Diene Monomer (EPDM) Rubber
- Natural Rubber (NR)
- Sulfur and Sulfur Compounds
- Silica
• Phenolic Resins
• Oil: Aromatic, Naphthenic, Paraffinic
• Fabric: Polyester, Nylon, etc.
• Petroleum Waxes
• Pigments: Zinc Oxide (ZnO), Titanium Oxide (TiO₂), etc.
• Carbon Black
• Fatty Acids
• Inert Materials
• Steel Wire

2.2.1 Compounding

While the finished tire contains many materials, the main ingredients in a rubber compound are the rubber and the filler (carbon black and silica), combined in such a way as to achieve different objectives. Depending on the intended use of the tire, the objective may be to optimize performance, to maximize traction in both wet and dry conditions, or to achieve superior rolling resistance. The desired objective can be achieved through careful selection of one or more types of rubber, along with the type and amount of filler to blend with the rubber. Rubber compounding is most likely the most difficult and complex process to master in the field of rubber technology as it is not really a science, but part art and part science. There is no infallible mathematical formulation to help the compounder; one must cope with literally hundreds of variables in materials and equipment. This is why compounding is so difficult a task (“Basic Rubber Compounding” 2014). For example, the make-up of tires varies depending on
tire type, truck or passenger car, and manufacture; possible combinations and resulting material variations are staggering. However, the basic materials are about the same, Table 2.1 (“Typical Tire Composition by Weight” 2014).

Table 2.1

Typical Tire Composition by Weight

<table>
<thead>
<tr>
<th>Passenger Tire</th>
<th>Truck Tire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber 14%</td>
<td>Natural Rubber 27%</td>
</tr>
<tr>
<td>Synthetic Rubber 27%</td>
<td>Synthetic Rubber 14%</td>
</tr>
<tr>
<td>Carbon Black 28%</td>
<td>Carbon Black 28%</td>
</tr>
<tr>
<td>Steel 14 – 15%</td>
<td>Steel 14 – 15%</td>
</tr>
<tr>
<td>Fabric, Fillers, Accelerators,</td>
<td>Fabric, Fillers, Accelerators,</td>
</tr>
<tr>
<td>antiozonants, etc. 16 – 17%</td>
<td>antiozonants, etc. 16 – 17%</td>
</tr>
<tr>
<td>Average Weight New: 25 lbs.</td>
<td>Average Weight New: 120 lbs.</td>
</tr>
<tr>
<td>Scrap: 20 lbs.</td>
<td>Scrap: 100 lbs.</td>
</tr>
</tbody>
</table>

Compounding can actually be broken into five separate main systems: elastomer system, filler system, protectants, processing aides and curing system (“Basic Rubber Compounding 2014). Each requiring its own specific compounding considerations.

With the elastomer system, while combinations can vary vastly, generally, four primary rubbers are used: natural rubber (NR), styrene-butadiene rubber (SBR), polybutadiene rubber (BR), and butyl rubber (including halogenated butyl rubber). The first three are primarily used as structural compounds such as tread and sidewall, while the non-permeable nature of butyl rubber and halogenated butyl rubber make them primarily suitable for the inner liner, or the inside portion that holds the compressed air inside the tire.
The most popular fillers are carbon black and silica; however, there are several types of each. Carbon black generally functions as a reinforcing filler with silica functioning primarily as an inert filler. The selection depends on the performance requirements, as they are different for the specific tire components, e.g. tread, sidewall and apex. Other ingredients and compounding also come into play to aid in the processing of the tire or to function as anti-oxidants, antiozonants, and anti-aging agents. In addition to the “cure package”—a combination of curatives and accelerators—is used to form the tire and give it its elasticity.

One important detail to note is that compounders use the unit of measure of "parts per hundred" (PHR) for their formula. This is a unit of weight for the relationship between the elastomer system and the other systems. If 100 parts of elastomer is utilized for all formulas then it is much simpler to change the other systems to create changes and different formulae. This is important since the cure system reacts only with the elastomer system; thus, as we change all the other systems, the relationship between the elastomer system and the cure system generally remains constant. Table 2.2 presents an example formula.
Table 2.2

Compound Formula ("Basic Rubber Compounding" 2014)

<table>
<thead>
<tr>
<th>FORMULA # RDXXX</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE POLYMER: XXX per ASTM D1418</td>
<td></td>
</tr>
<tr>
<td>5BG 515 A14, B14, C12, F19 Z=DUROMETER 55A per ASTM D2000</td>
<td></td>
</tr>
<tr>
<td>SPECIFIC GRAVITY: X.XXX</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>PHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer, Primary</td>
<td>90.00</td>
</tr>
<tr>
<td>Polymers, Secondary &amp;/or liquid</td>
<td>10.00</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>1.00</td>
</tr>
<tr>
<td>Antiozonants, static &amp;/or dynamic</td>
<td>1.00</td>
</tr>
<tr>
<td>Reinforcing fillers (Black &amp;/or Non-black)</td>
<td>35.00</td>
</tr>
<tr>
<td>Semi &amp;/or non-reinforcing fillers (Black &amp;/or Non-black)</td>
<td>25.00</td>
</tr>
<tr>
<td>Plasticizer, Liquid or DLC (high and/or low temp)</td>
<td>15.00</td>
</tr>
<tr>
<td>Process aid, mixing</td>
<td>1.00</td>
</tr>
<tr>
<td>Adhesion promoter</td>
<td>5.00</td>
</tr>
<tr>
<td>Activator(s)</td>
<td>5.00</td>
</tr>
<tr>
<td>Inhibitors, (UV, flame, flex cracking, static, etc.)</td>
<td>1.50</td>
</tr>
<tr>
<td>Process aid, molding</td>
<td>3.00</td>
</tr>
<tr>
<td>Tackifier</td>
<td>1.50</td>
</tr>
<tr>
<td>Colorants</td>
<td>1.50</td>
</tr>
<tr>
<td><strong>MB SUBTOTAL</strong></td>
<td><strong>195.50</strong></td>
</tr>
<tr>
<td>Vulcanizer (Sulfur, Peroxide or other)</td>
<td>2.00</td>
</tr>
<tr>
<td>Accelerator, primary</td>
<td>1.50</td>
</tr>
<tr>
<td>Accelerator, secondary</td>
<td>1.00</td>
</tr>
<tr>
<td>Accelerator, ultra</td>
<td>0.25</td>
</tr>
<tr>
<td>Accelerator, sulfur donor</td>
<td>1.50</td>
</tr>
<tr>
<td>Retarder, scorch</td>
<td>0.50</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>202.25</strong></td>
</tr>
</tbody>
</table>

After determining the desired formula the next operation is mixing of materials selected. Mixing operations are typically three to five minute batch processes of
approximately 200 kilograms of rubber compound. The mixer functions to break down the rubber, fillers and chemicals and mix them with other ingredients.

Order of addition of ingredients is critical, as is the mixing temperature, which can rise as high as 160 - 170°C. Excessive temperature can damage the compound; therefore, the mixing operation is typically a two stage operation adding the curative package in the final stage of mixing, and controlling the final mixing temperature at less than 100-110°C to prevent scorching.

Upon completion of the mixing process the batch is dumped out of the mixer and sent through a series of machines to form it into a continuous sheet called a “slap.” Slap is transferred to other areas for preparation of specific tire components to include: bead wire assembly, innerliner calendaring, steel and/or fabric belt/ply cord calendaring, tire sidewall extrusion, and tire tread extrusion.

2.2.2 Production of Pneumatic Tires

Production of a pneumatic tire consists of three primary steps: preparatory, component construction and building and inspection. Preparatory step includes the compounding process discussed previously in addition to selection and preparation of fabric and steel cords. Component construction consists of construction and cutting of fabric cords and steel belts, bead assembly, extrusion of the tread and sidewalls and construction of the innerliner. The final step of building and inspection involves the actual building of the tire, from the components as prepared in the component construction step, high pressure-high temperature molding and curing and finally a series of visual, mechanical and instrumental inspections.
2.2.2.1 Construction and Cutting of Fabric Cords and Steel Belts

Since tires are required to carry heavy loads, steel and fabric cords are used in their construction to reinforce the rubber compound and provide strength. Typical materials suitable for tire cord production include cotton, rayon, polyester, aramid, fiberglass, and steel. A calendaring process is used to produce fabric or steel belts in which the rubber compound is pressed onto the fabric or steel cords. A pre-set number of fabric or steel cords under proper tension are continuously pressed through two steel rollers (calendar), and rubber compound is added to the opening area between the rollers. Then the rubber compound is pressed into, on top of and on the bottom of the fabric or steel cords. A continuous sheet of cord-rubber composite goes through several more rollers to ensure good penetration and bonding between the rubber and cords as this is a critical step to performance due to the importance of bonding of the fabric or steel cord material to the rubber. Sheet thickness, spacing between cords, the number of cords and penetration of rubber into the composite sheet are a measure of quality. After calendaring the composite sheet is cut into appropriate sizes, shapes, and angles depending on the desired contour of the tire.

2.2.2.2 Bead Assembly

The bead component of the tire is a rigid composite loop that strengthens and supports the body plies and secures the tire onto the wheel assembly. Included in the tire bead component are the steel wire loop, apex or bead filler; the chafer, which protects the wire bead components; the chipper, which protects the lower sidewall; and the flipper, which helps hold the bead in place. The two primary components of the bead component
are the bead wire loop and the bead filler which are assembled on sophisticated precision machinery. The bead wire loop is made from a continuous steel wire covered by rubber and wound around with several continuous loops. The bead filler is made from a very hard rubber compound, which is extruded so as to form a wedge. The most critical attribute of the bead component is the precision of the bead circumference. If too small, tire mounting can be a problem; but if too loose, the tire can come off the rim too easily under loading and cornering conditions. After proper assembly of all components and circumference measurement, the bead component is ready for the tire building operation.

2.2.2.3 Tread and Sidewall Extrusion

Most of the rubber compounds produced in the mixing operation are processed through an extruder making extrusion one of the more important operations in the tire manufacturing process. Various components for the tire building operation such as tread, sidewalls and apex are prepared for the tire building process by forcing uncured rubber compounds through an extruder to shape the tire tread and sidewall profiles.

Modern tire manufacturing utilizes a computer-controlled cold feed screw-type extruder consisting of an extruder barrel and extruder head. Rubber compound is fed cold into the extruder barrel where it goes through heating, blending and pressurization. The heated blended rubber then flows to the extruder head where it is shaped under pressure.

The portion of the tire that comes in contact with the road is known as the tire tread. The tread consists of tread itself, tread shoulder, and tread base. Consisting of at least three different rubber compounds the complex tread profile requires a combination
of three different extruders sharing an extruder head. Three rubber compounds are extruded simultaneously from different extruders merged into a shared extruder head. A die plate at the exit of the extruder head forms the shape and dimensions and then the tread assembly is cooled through a long cooling line to control and stabilize the dimensions. At the end of the cooling line the tread is cut according to a specific length and weight for the tire being built.

The tire sidewall is extruded in a way similar to the tire tread component; however, its structure and the compound used are quite different from tread. Sometimes the sidewall extrusion process can be more complicated, as four extruders may be needed; for example, when building a tire with white sidewalls or with white lettering on the sidewalls.

### 2.2.2.4 Construction of the Innerliner

The inner-most layer of the tire is the innerliner which functions to retain the compressed air inside the tire and maintain tire pressure. As previously mentioned butyl rubber or halogenated butyl rubber are used in the innerliner compound due to low air permeability. The innerliner is produced using the calendaring process to provide a thin layer constant thickness film without surface defects to ensure retention of air pressure. As with the extruded tread, the proper length of innerliner sheet is pre-cut to be ready for the tire building process.
2.2.2.5 Tire Building, Curing and Inspection

At this point, the tire is ready to be built which is usually accomplished by highly robotized machinery to ensure quality and efficiency. All components described are assembled and the building process begins.

A radial tire building process typically involves a two-stage process on a flat drum. The first stage consists of successively layered wrapping of the drum with the innerliner then first body ply followed by the second body ply. Next, the bead assemblies are positioned and covered by the body plies due to force applied by a bladder on the drum that is inflated and pushed in from both ends of the drum. The final process in this stage involves pressing the sidewall sections onto both sides.

In the second stage of the building process the belts, nylon cap and tread are applied on top of the structure built in the first stage. While at this point the product is beginning to look like a tire, a curing process must be completed.

In addition to molding of the sidewalls and tread, the final curing of the rubber compounds occurs through a series of chemical reactions. Curing is a high-temperature and high-pressure batch operation involving placing the uncured tire into a mold at a specified temperature. The mold is closed allowing the rubber compound flow and mold the shape of the tire and form the final tread and sidewall details. During the entire process the mold cannot be opened until the curing reaction is completed.

Inspection is the final step in the manufacturing process and is important in ensuring quality with respect to performance and safety. Inspection begins with continuous in-process visual inspect followed by a series of mechanical (balance, force and moment) and instrumental (X-Ray) methods to ensure structural integrity.

2.3 Post-Consumer Waste Products and Processes

Post-consumer waste is waste produced by the end use consumer of a material stream. In other words, post-consumer waste is simply garbage or materials generated from garbage that individuals routinely discard. Post-consumer waste is considered to be different than pre-consumer waste, or manufacturing waste which is reintroduced back into the manufacturing process. Pre-consumer waste, commonly used in manufacturing industries, is not considered a recycled material in the traditional sense.

The focus of this work is on post-consumer waste, specifically polymers reclaimed from waste pneumatic tires.

2.3.1 Waste Tire Issue

Large amounts of polymers, such as natural rubber, synthetic rubber, ethylene-propylene diene monomer, and butyl rubber, collectively referred to as rubber, are used in production of pneumatic tires for passenger cars, trucks, airplanes, etc. When these tires are not serviceable and discarded, only about 1% or less rubber has been lost due to abrasion wear. Almost the entire amount of original rubber from a waste tires is discarded, which requires a very long time for natural degradation.
One of many issues facing society today is the problem of waste management. Disposal of waste polymers is a serious environmental concern as polymeric materials do not decompose easily. This poses two major problems: waste of valuable rubber and environmental pollution due to disposal of waste tires (Kandhal 1992, Adhikari 2000).

According to the U.S. Environmental Protection Agency (EPA), there are at least 275 million waste tires in stockpiles throughout the United States. In addition, hundreds of millions of waste tires are generated annually ("Waste-Resource Conservation" 2013). EPA estimates that approximately 290 million waste tires were generated in 2003 alone, and that one waste tire per person is currently being generated each year in the United States. Tires that are not beneficially reused either end up occupying valuable landfill space, or worse, are illegally disposed of in streams, fields, woodlands, or other areas harmful to the environment and public health. Two major approaches to solve this problem are recycle and reuse of used and waste rubber, and reclamation of rubber raw materials.

In 2003, markets for scrap tires were consuming 233 million, or 80.4%, of the 290 million annually generated scrap tires. Scrap tires are used in a number of productive and environmentally safe applications. From 1990 through 2003, the total number of scrap tires going to market increased from 11 million (24.5%) of the 223 million generated to 233 million (80.4%) of the 290 million generated ("Waste-Resource Conservation" 2014).

Currently, scrap tires are used in a number of productive and environmentally safe applications (Amari et al. 1999). In 2013, markets for scrap tires were consuming 3666 thousand tons, 95.9%, of the estimated 3824 thousand tons of scrap tires generated.
annually. The three largest scrap tire markets in 2013 were: tire derived fuel (TDF), 55.4%, civil engineering applications including tire shreds used in road and landfill construction, septic tank leach fields and other construction applications, 4.5%, and ground tire rubber (GTR) applications, 25.5%, 975 thousand tons or approximately 60 million scrap tires, of which rubberized asphalt represents 7%, approximately 68 thousand tons or 4.2 million scrap tires (“Scrap Tire Markets” 2014).

2.3.2 Waste Tire Collection

The process of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products is commonly referred to as recycling with these materials considered as recyclables. There are several methods for collecting common recyclables, including curbside collection, drop-off centers, and deposit or refund programs. After collection, recyclables are usually sent to a recovery facility to be sorted, cleaned, and processed into materials that can be used in manufacturing. Processed recyclable materials are bought and sold as raw materials for manufacturing with prices fluctuating depending on supply and demand (Owen 1999).

A federal program for disposal of scrap tires as solid waste in the U.S. is non-existent. Scrap tire solid waste is regulated primarily by state governments with Minnesota pioneering scrap tire solid waste management in 1985 through enactment of state law. Since then scrap tire solid waste management laws have been enacted by most state governments. Though states have their own program, there are common features: source of funding for the program; licensing or registration of scrap tire haulers, processors, and end users; manifests for scrap tire shipments; limitations on who may
handle scrap tires; financial assurance requirements for scrap tire handlers; and market development activities (“Waste-Resource Conservation” 2014). Some state programs and recycling efforts are often supported by “tipping fees” charged to the consumer at purchase or disposal of each tire. Comparative higher charges for disposal to “tipping fees” tend to discourage landfill disposal and encourage more affordable recycling programs.

Municipalities help educate the public about illegal dumping and enforce anti-tire dumping laws. Some local jurisdictions encourage proper disposal by allowing local citizens to drop off limited numbers of tires at recycling centers, or conduct tire amnesty days where local citizen can bring limited numbers of tires to drop-off sites free of charge. Tire recycling centers are either fixed collection sites located adjacent to or at facilities where other solid wastes are managed such as dumpster locations, transfer stations, waste disposal sites, or municipal solid waste landfill sites, developed and maintained in a manner to prevent waste tires from being contaminated with dirt, mud, rocks, etc. which could lead to problems in further processing. Additionally, mobile collection units utilizing mobile trailers or other units located at one fixed location throughout the year or moved between various fixed locations, may be used to provide all residents equal opportunity to dispose of tires.

2.3.3 Waste Tire Processing

The first market for whole scrap tires is retreading which involves removing the worn tread and adding a new tread (“About Retreading” 2014). This process offers not only environmental benefits but economic benefits as it saves millions of gallons of oil
each year, requiring about a third of the oil resources to retread compared to production of a new tire, while providing quality, comfort and safety comparable to new tires at 30 to 70 percent of the cost. Most retread tires are used by the trucking, aircraft, construction and agricultural industries. Approximately 24 million tires are retreaded and sold each year in the US and Canada. These tires are not included in the estimated 290 million annual tires reported by the EPA (“Waste-Resource Conservation” 2014). Many scrap tires are exported to foreign countries to be reused as retreads, especially in countries with growing populations of automobile drivers such as Japan and Mexico. According to Mexico’s National Association of Tire Distributors, as many as 20% of tires sold in Mexico are imported as used tires from the US and then retreaded for reuse.

Whole tires may also be recycled or reused as highway crash barriers, for boat bumpers at marine docks, and for a variety of agricultural purposes.

Scrap tires may be recycled by cutting, punching, or stamping them into various rubber products after removal of the steel bead. Products include floor mats, belts, gaskets, shoe soles, dock bumpers, seals, muffler hangers, shims, and washers.

Reclamation of waste rubber from tires for the three largest uses of waste tires, previously mentioned, often requires reduction of particle size or increase in surface area. Grinding processes for tire rubber are well developed and widely used for recycling of tire rubbers and rubber wastes. Industrial machines are available for breakup and separation of rubber from steel, cord, and fabrics that are present in tires. High industrial rates for production of tire rubber crumbs have been achieved.

The most common method of size reduction is via one of two grinding processes: ambient grinding and cryogenic grinding. A third method, wet grinding has been used,
but is not common (Harshaft 1972). In these grinding processes GTR is produced from whole scrap tires through mechanical shearing and grinding resulting in size-reduced rubber or crumb tire rubber. In the crumb tire rubber market there are two classes of particle size: “ground” rubber (referred to herein as GTR) which is 2.0 mm (10 mesh) and smaller and “coarse” rubber which is larger than 2.0 mm (10 mesh), with a maximum size of 12.75 mm (0.5 inch). Typical sizes of reduced rubber used in modified asphalt binders for road construction ranges from about 1.5 mm (1500µm) down to 420µm (15 mesh to 40 mesh) with limited use sizes as small as 177µm and 125µm (80 mesh and 120 mesh).

The size reduction tire reclamation process begins by first reducing Vulcanized scrap rubber to 50 x 50 millimeter or 25 x 25 millimeter chips. After which a magnetic separator and a fiber separator (cyclone) remove all of the steel and polyester fragments. These waste rubber chips can then be further reduced using an ambient ground mill, or it can be ground into finer particles while frozen using cryogenic grinding (Klingensmith & Baranwal 1998).

Ambient mechanical size reduction often uses conventional high powered rubber grinding mills or rubber “cracker” mills set at a close nip. Using this relatively inexpensive method vulcanized rubber is sheared and ground into small particles in the -10 to -30 mesh range which is considered to be a relatively large particle size; therefore, multiple grinder passes can be used to further reduce the particle size with the lower particle limit being a -40 mesh particle. The ambient, multiple pass, grinding process generates a significant amount of heat which can degrade the rubber and if the rubber is not properly cooled combustion may occur upon storage. Szilard reported that the
ambient grinding process produces an irregularly shaped particle with many small hair-like appendages. These appendages are believed to attach to the virgin rubber matrix producing an intimate bonded mixture when ambient ground waste GTR is compounded with virgin rubber in new materials (Szilard 1973). Similarly, performance differences of ambient ground over cryogenic ground rubber in GTR modified asphalt binders may also be attributed to the particle characteristics described by Szilard.

Cryogenically ground rubber can also produce particles in the -10 to -40 mesh range similar to ambient grinding; however, use of liquid nitrogen to cool the scrap rubber below its glass transition temperature and then pulverizing the brittle materials allows for much finer particles in the -60 to -140 mesh range. With the exception of inexpensive rubbers, such as tire rubbers, the cryogenic process is not economical because of the expense of substantial quantities of liquid nitrogen or other cryogenic liquids used to freeze the rubber (LaGrone 1986). Another significant feature of the cryogenic process is that almost all fiber or steel is liberated from the rubber, resulting in a yield of usable product and little loss of rubber (Klingensmith & Baranwal 1998).

The wet grinding method is said to achieve a crumb fineness of approximately -200 mesh (Lynch & LaGrone 1986). In fact, wet or solution process grinding can yield a very small particle size, ranging from -400 to -500 mesh. The advantage of fine particle wet ground rubber is that it allows good processing, producing relatively smooth extrudates and calendared sheets when compounded with virgin rubber in new materials (Lynch & LaGrone 1986).

Scrap tires may also be imported by some foreign countries tires to be shredded and used as crumb rubber, or to be used as fuel. An unfortunate downside of exporting
scrap tires is that receiving countries may end up with a disproportionate volume of tires, in addition to their own internally-generated scrap tires, therefore, not all exported tires will be reused or recycled.

2.4 Comparison of Post-Consumer to Synthetic Polymers

For this work polymers are grouped into two broad classes of pre-consumer and post-consumer polymers. Pre-consumer polymers are polymers that have not been previously used for production of consumer goods or end products e.g. pneumatic tires and post-consumer polymers are polymers that have been recovered from post-consumer waste for repurpose or reuse, e.g. GTR. The following discussion will provide a better understanding of polymers in general.

Polymers derived from the Greek poly and meros respectively meaning “many” and “parts,” are large molecules composed of repeating chemical units referred to as a mers. (Seymour et al. 1981). Polymer molecules are manifest in linear, branched or networked structures know as morphologies. Linear, branched and networked polymers are thermoplastic; however, some networked or three-dimensional (cross linked) polymers are thermoset polymers. For perspective, polymer chains can be depicted as ropes Figure 2.1. Using the rope comparison, a linear polymer with a polymer chain of 10,000 units (a typical length), a standard half-inch-thick rope would be about 128 meters (140 yards) long to represent the length-to-thickness ratio of the microscopic polymer molecule.
Chemists and chemical engineers regularly involved in some phase of polymer technology often refer to this as the polymer age. Matter was classified by the ancient Greeks as animal, vegetable and mineral. While mineral matter was highly studied by alchemists and medieval artisans, for the most part, largely polymeric animal and vegetable matter have always been more important. In fact, protein, basic to life itself, was and is the source of amino acids and energy as well as being the first polymer. Thus we have actually always lived in a polymer age.

Prior to the 1800s polymers would have been naturally occurring materials such as cotton, flax, and silk fibers; bitumen caulking materials; glass and hydraulic cement; leather and cellulose sheets (paper); natural rubber and shellac. It can be assumed that the synthetic polymer age began in the early 1800s with vulcanization of rubber by Charles Goodyear in 1839 with development of polymer technology being extremely rapid in the 1940s and with science often being proceeded by art. Some scientists maintain that naturally occurring polymers, or biopolymers, and synthetic polymers should be classified and studied separately. Some prefer to use the word macromolecule
or large molecule, instead of polymer to address other than synthetic polymers; however, the same principles apply to all polymers so the terminology of natural polymers and synthetic polymers will be used herein.

Pre-consumer polymers are generally of either natural origin or synthetic origin while post-consumer polymers may be either/or, or combinations of both, to which other compounds or processes may have been added or performed, which is generally the case of post-consumer polymers from reclamation of polymers from scrap tires or GTR.

2.4.1 Properties of Common Synthetic Polymers

Morphology, the study of form and structure of polymers, from the Greek “study of shape is important in understanding polymer properties. Morphology, as well as properties, is dependent on many factors including inter- and intra- chain bonding, the nature of the backbone, processing events, presence/absence of additives including other polymers, chain size and geometry, and molecular weight distribution. For example, the critical chain length required for the onset of entanglement is dependent on the polarity and shape of the polymer. While paraffin wax and high density polyethylene (HDPE) are homologs with relatively high molecular weights, the chain length of paraffin is too short to permit entanglement hence it lacks the strength and other characteristic properties of HDPE (Seymour 1981). The melt viscosity of a polymer is often found to be proportional to a power function of the critical chain length regardless of the structure of the polymer.

Most materials have melting/freezing and boiling/condensing points, however, polymers do not boil because the energy necessary to put a polymer into the vapor state is
greater than the bond energies of the atoms that hold the polymer together, and thus they degrade prior to boiling.

The temperature where polymer units or segments can move but the entire chain cannot is the glass transition temperature ($T_g$). In order for a polymer to be flexible, its various units or segments must be able to move. Flexibility of amorphous polymers above the glassy state is dependent on a wriggling type of segment motion in the polymer chains. Most vinyl polymers have $T_g$ values below room temperature so that they appear to be flexible and act as rubber and plastic materials. Most polymers formed through a condensation reaction, condensation polymers, have $T_g$ values above room temperature and are used as hard plastics and fibers. A polymer's melting point ($T_m$), greater than the $T_g$, is the temperature where entire chain movement occurs. Values of $T_m$ are usually 33 to 100% greater than $T_g$ with symmetrical polymers like high density polyethylene (HDPE) exhibiting the greatest difference between $T_m$ and $T_g$. Values of $T_g$ are generally low for elastomers and flexible polymers and relatively high for hard amorphous plastics.

Many polymers are themselves brittle at room temperature. For these polymers to become more pliable, additives called plasticizers that allow segmental mobility, and consequently segmental flexibility, are added. Plasticizers are added to synthetic polymers such as polyvinyl chloride (PVC) and polystyrene (PS) allow the polymers to be flexible.

The inflexible regions of a polymer, or crystalline regions, are often referred to as "hard" regions. Flexible regions of a polymer, where segmental mobility occurs, are referred to as "soft" regions. This combination of hard and soft can be illustrated with
common polymers used in asphalt modification, specifically styrene-butadiene-styrene block copolymers (SBS). The polystyrene (S) portion of such polymers is considered "hard," while the polybutadiene (B) portion, flexible at room temperature, is considered "soft."

Physical properties of polymers are related to the strength of covalent bonds, the stiffness of segments in the polymer backbone and strength of intermolecular forces between the polymer molecules. The strength of the intermolecular forces is equal to the cohesive energy density (CED), which is the molar energy of vaporization per unit volume. CED values may be used to predict solubility since intermolecular attractions of solvent and solute must be overcome when a solute dissolves. Polymers dissolve in two steps: the first step is a slow swelling process called solvation in which the polymer swells by a factor related to CED. Linear and branched polymers dissolve in a second step, but network polymers remain in a swollen condition.

2.4.2 Properties of Ground Tire Rubber

Materials that stretch and recover or compress and rebound are often called rubbery materials or rubber, such is the case of compounds used to produce pneumatic tires. In actuality the only true rubber is natural rubber from the latex of nearly 2000 different plants, more specifically the only important commercial source of natural rubber is latex from the Hevea brasiliensis (hevea rubber) tree. Natural rubber is a primary source of poly(isoprene) though synthetic poly(isoprene) is also available.

The Goodyears, Charles and Nelson, converted a thermoplastic elastomer to a thermoset elastomer and a hard thermoset plastic by addition of small and large amounts
of sulfur crosslinks respectively (Seymour 1981). Charles transformed the heat-
softenable thermoplastic hevea rubber to a less heat-sensitive product by using sulfur to
form a relatively small number of connecting links or cross links between the long
individual poly(isoprene) chainlike molecules (vulcanized rubber). Nelson used sulfur to
produce many cross links between the poly(isoprene) chains so that the product was no
longer thermoplastic but was a thermoset plastic (ebonite).

What Charles Goodyear discovered, was that when he mixed sulfur and heat with
natural rubber, it changed from a material, natural rubber, that became sticky and soft on
hot days and that wouldn’t return to its original shape when stretched or compressed, to a
material that returned to shape and remained relatively unchanged in the hot weather.
The process of Goodyear’s discovery is now known as “Vulcanization,” named after
Vulcan, the Roman god of fire.

To provide the reader a better understanding the process of vulcanization and
properties of GTR a short discussion of vulcanization is of benefit (Kumar et.al 1997).
Figure 2.2 will be used to facilitate this discussion:

Figure 2.2

Vulcanization of Natural Rubber (Poly(isoprene))
The left hand side of the chemical reaction presented in Figure 2.2 shows the structure of poly(isoprene) with the repeating unit of the isoprene in brackets, \( n \) represents the number of repeating units in the chain, e.g. 10,000. In the bracketed isoprene structure, the middle of the isoprene unit exhibits two carbon atoms linked together with two bonds while all the other bonds are singular. In organic chemistry, these are referred to as single or double bonds in. In two ways these double bonds are what allow elastomers to be elastic. First it allows the repeating units to rotate about the single bonds giving the molecule flexibility. Second, the double bond is not very stable. With sufficient heat energy double bonds can be reduced to single bonds by disconnection of one of the bonds from one of the double bond carbon atoms. Double bonds in macromolecules are referred to as being "unsaturated." Unsaturated double bonds are common to most synthetic elastomers. If one of the bonds is disconnected from one of the carbon atoms an open site is available to attach to a different atom. Therefore, all of the double bonds are considered potential reaction sites. In the case of vulcanization, when elemental sulfur is combined with rubber, the disconnected site will attach to a sulfur atom as depicted in yellow on the right hand side of Figure 2.2.

Sulfur attaching to a single potential reaction site is not of much value; however, if that same sulfur atom attaches to a similar site on another poly(isoprene) molecule beneficial improvements can occur in the poly(isoprene) molecules involved in the reaction. This reaction in known as sulfur "crosslinking" of poly(isoprene) and is the primary mechanism of Goodyear’s vulcanization.

To better understand how the double bond helps give elastomers their elasticity we will employ the rope analogy used previously. In this example, rather than one rope,
think of a basket of ropes of the same length; where the individual rope strands cross one another is an example of where vulcanization may occur, Figure 2.2. Vulcanization or cross link reactions where the strands of polymer molecules cross is what gives elastomers, e.g. vulcanized rubber, their elasticity. As we try to slip the strands of rope apart the crosslinks resist the movement and forces the strands back to their original position after the applied stress is relieved. Sulfur crosslinks occur at approximately one out of every 200 potential sites in an average sulfur vulcanization system. It is important to note at this point that all double bonds are not involved in the vulcanization process and the remaining unsaturated double bonds play an important role in the elastic properties of the final rubber product.

Due to the chemical nature of sulfur, reaction sites may contain single or multiple sulfide atoms in the sulfur cross links between the poly(isoprene) strands. When one sulfur molecule exists in the cross link of polymer chains it is referred to as “monosulfidic” two sulfur molecules in the cross link are referred to as “disulfidic” and greater than two sulfur molecules is referred to as “polysulfidic.” All vulcanized rubber will contain some of all of the above types of vulcanized crosslinks. The ratio of one type of crosslink versus the others varies with curing system used the vulcanization process and has an influence on the physical properties of the final rubber product. For example, highly efficient curing systems yielding a large number on monosulfic crosslinks will provide for improved heat aging and compression set resistance but will give up low temperature crystallization resistance and higher extension ratios as compared to curing systems of lesser efficiency yielding greater bisulfidic and polysulfidic cross links. Additionally, the stability of the monosulfidic cross link is much
greater than bisulfidic and polysulfidic cross links due to the stronger covalent carbon-
sulfur bonds as compared to the weaker sulfur-sulfur bonds.

On occasion reference may be made to “devulcanized” rubber in the rubber
reclaiming and recycling industry, however, “devulcanization” is technically a misnomer,
since vulcanization is irreversible, Figure 2.3.

Figure 2.3

Vulcanization is a Non-Reversible Reaction

The term is used to describe the softening of a vulcanizate caused by heat and
chemical additives during reclaiming (Hawley 1981). Warner defines “devulcanization”
in sulfur cured rubber as the process of cleaving, totally or partially, the poly-
di- and monosulfide crosslinks which were formed during the initial vulcanization (Warner
1994). In this case “devulcanization” might be more accurately referred to as
desulfurization.

“Devulcanization” of rubber has been continually researched by the rubber
industry as well as other industries for a number years (McCoy 2015). At issue has been
“devulcanizing” the rubber without compromising its desirable properties of the resulting rubber. Typically the process has involved treating rubber in granular form with heat and/or softening agents in order to restore its elastic qualities, thereby enabling the rubber to be reused. Referring back to Figure 2.2 it can be seen that not all of the double bonds in the poly(isoprene) have been reacted with sulfur and that the resulting cross linked poly(isoprene) contains a number of unsaturated double bonds. As discussed it is these double bonds that allow the polymer to be elastic. Attempts to “devulcanize” vulcanized rubber often destroys these more reactive double bonds thereby destroying the desired elastic functionality provided by the available double bonds.

Several experimental processes have achieved varying degrees of success in the laboratory, but have been less successful when scaled up to commercial production levels. (Lloyd 2004). Additionally, different processes result in different levels of “devulcanization.” For the most part recycling of “devulcanized” rubber into production of new pneumatic tires has been restricted to low speed tires such as tires for farm and construction equipment.

2.5 Post-Consumer Uses of Ground Tire Rubber

The market for GTR has been growing over the past several years. As previously discussed in section 2.3.3, there are two classes of particle sizes in sized reduced rubber: “ground” rubber (10 mesh and smaller) or GTR and “coarse” rubber (larger than 10 mesh, with a maximum size of one-half inch). While GTR is used in a growing number of products and applications GTR modified asphalt is the largest single market for GTR, consuming an estimated 220 million pounds, or approximately 12 million tires annually.
The growing number of diverse markets and end-use applications for tire derived reduced size rubber includes but is not limited to: athletic surfaces (running tracks, tennis courts, basketball courts, etc.); athletic fields (soccer, football, baseball, etc.); playground and safety surfaces; landscaping, trails and walkways; equestrian surfaces (paddocks, stables, etc.); molded and extruded articles and products; automotive parts and accessories; and modified asphalt sealants and emulsions (Kandhal 1992, Myhre et al. 2002).

2.6 Modification of Asphalt Binders

Asphalt modification is an historical concept, technologists have used modification methods to improve properties of bitumen for desired end use characteristics for about as long as bitumen has been used. Information provided in this section is primarily sourced from IS230 The Bitumen Industry – A Global Perspective: Production, chemistry, use, specification and occupational exposure, a joint publication of the Asphalt Institute and Eurobitume of which the author had primary responsibility in writing the section on bitumen modification, (IS230 2015).

2.6.1 Why Modify Asphalt Binders

Asphalt binders are generally specified according to desired end use product performance characteristics with limits bounded by high and low temperature performance requirements. Upper and lower performance extremes define an asphalt binder’s performance range, Figure 2.4 (Meynard 1981).
Figure 2.4 presents a plot of temperature on the ordinate versus stiffness on the abscissa. From figure 2.4 it can be seen that asphalt binders exhibit different states with respect to temperature. Below the low temperature limit, e.g. glass transition temperature, $T_g$, or brittleness temperature, $T_{frass}$, asphalt exists as a glassy solid or in an elastic state. Above the high temperature limit, e.g. softening point temperature $T_{sp}$, asphalt exists as a viscous liquid or in a viscous state. The two changes in state described with respect to temperature, low temperature limit and high temperature limit, define the “performance range” of an asphalt binder, where the binder exists in a visco-elastic state. The specific temperatures where a binder meets specific low temperature and high temperature limits define what is commonly called the useful temperature interval (UTI), Figure 2.5 (Meynard 1981).
The final asphalt product is produced to meet product specifications, either directly in the refining process, or by blending asphalts with different physical properties. Blending may take place at the refinery, at terminals, or at a third-party facility where blend components and finished products can be easily transported by truck, rail, or barge to their final locations. Higher viscosity products or asphalt binders may be blended with lower viscosity products or asphalt binders in suitable proportions to satisfy final product specification requirements. The range of performance with respect to upper and lower temperature boundaries is typically inherent to the specific crude from which an asphalt is derived; therefore, hardening or softening the binder through refining processes or blending of harder and softer components from the same crude oil tends to shift both UTI limits in the same direction by the same amount at the same time. In other words, the entire UTI shifts right or left respectively to hardening or softening of the asphalt binder.

Often the desired spread of temperature boundaries exceeds the inherent range of available asphalt performance achievable by simple asphalt blending and may require
that the asphalt be modified in a number of acceptable manners. Modification simply put is a method used to widen the UTI of asphalt binders by shifting the high and low temperature limits of the UTI independently, Figure 2.6.

![UTI of Modified Asphalt Binders](image)

Figure 2.6
UTI of Modified Asphalt Binders

### 2.6.2 Asphalt Binder Modification Processes

While asphalt is usually used in neat form without additives, it can be modified through addition of non-bituminous components or other processing methods in order to provide products with different physical properties required for desired performance, or mode of application. Modification techniques are primarily dependent on the desired performance of the final product. Typical methods include but are not limited to four general classifications: addition of special fillers or extending agents, chemical modification, air oxidation and polymer modification. The main topic of this work relates to polymer modification so the remaining methods will only be mentioned briefly.
2.6.2.1 Special Fillers and Extending Agents

Addition of special fillers or extending agents is likely the oldest method of bitumen modification used to improve stiffness and viscosity characteristics including additives such as:

- Mineral Fillers (e.g. limestone, fly-ash and clay)
- Fibers (e.g. natural - cellulose, synthetic - polypropylene)
- Natural Asphalts (e.g. Trinidad Lake Asphalt, Gilsonite)
- Adhesion Promoters (e.g. hydrated lime)
- Petroleum Distillates (e.g. naphtha, white spirits, Kerosene, gas oil)
- Emulsifiers (e.g. fatty amine derivatives, tall oil soaps)
- Residues from re-refining of waste engine oil (Refined Engine Oil Bottoms (REOB))
- Waxes (e.g. synthetic such as Fischer-Tropsch, natural such as Montan and amide derivatives such as Ethylene Bis-Stearamides)
- Bio-binders (e.g. vegetable based components, animal by-products and waste)
- Warm Mix systems (e.g. synthetic and natural waxes)

Petroleum distillates can range from 5% to as much as 40% of the final blended material depending on the performance properties being targeted. According to Mundt, et al. petroleum distillates are the most widely used additive blended into bitumen for paving applications. In the past other materials (such as light cycle oil, catalytically cracked clarified oil, and coal tar derived material) have reportedly been blended with bitumen to produce bitumen products.
If used, re-refined engine oil bottoms are typically present at 5% to 10% by weight of the binder. Localized use of REOB materials has been known for more than 20 years in the United States. In the past the main use for waste lubricating oils was as an industrial fuel. More recently, economic incentives to re-refine waste drain oil to produce base oils have led to an increase in the volumes being re-refined. As a result there have been increased incentives to utilize these materials in bitumen. Little systematic research into the performance of pavements produced with REOB containing binders has been conducted. These materials can contain a number of contaminants introduced during the use of engine oils.

2.6.2.2 Chemical Modification

Chemical modification and oxidation are often used to address specific performance characteristics such as moisture resistance and temperature susceptibility. Oxidation has been covered previously, additional chemical methods may include:

- Adhesion Promoters (e.g. fatty amine derivatives, imidazolines)
- Phosphorous Compounds (e.g. phosphorous pentoxide, polyphosphoric acid)
- Elemental Sulfur
- Maleic Anhydride
- Warm Mix systems (e.g. Utilizing surfactants or chemical lubricating additives)

Adhesion agents are generally utilized at levels below 1%, as are many of the warm mix systems based on additives blended into the bitumen.
Sulfur in some processes constitutes only a minor amount (<1%) to and is used to cross link styrene-butadiene polymers, but may comprise up to 40% by total binder weight when used to produce a sulfur extended asphalt. Concerns regarding evolution of hydrogen sulfide (H₂S) and other sulfur compounds during initial construction and during recycling have slowed the adoption of sulfur as a bitumen additive.

2.6.2.3 Oxidation and Air Rectification

Oxidized asphalt, commonly known as blown asphalt or air blown asphalt, is made in a refinery unit referred to as the asphalt blowing still or air blowing unit (ABU) or simply the oxidizer. Depending on the feedstock viscosity and the processing conditions, the ABU produces two types of product with distinctly different characteristics: air rectified or semi-blown asphalt and oxidized or blown asphalt.

The processes involve passing air through an asphalt feedstock at elevated temperature in order to harden the asphalt by increasing its softening point and changing the temperature-viscosity properties of the asphalt. The processes achieve this through varying degrees of chemical reactions which result in an increase in the average molecular weight of the asphalt leading to higher viscosity asphalt.

Air rectification is commonly used to adjust the physical properties of a given feed in order to produce binders used to make products used in paving. Air rectified products are used in the same manner as vacuum distilled asphalt binders. Air-rectified binders may be used in paving as well as some roofing applications, such as shingle saturants and American Society for Testing and Materials (ASTM), D 312 Type I, built-up roofing asphalt (BURA), and also for some industrial applications.
Oxidation, is used to adjust the physical properties of a given feed, generally very soft flux, in order to manufacture substances used to make products for roofing, such as ASTM D 312 Type III BURA, and for some industrial applications. Flux oils may be used to soften the feed to the ABU and catalysts may also be used to increase or decrease the speed of reaction and improve temperature susceptibility relative to oxidation without a catalyst. Catalysts include materials such as ferric chloride, (FeCl), hydrochloric acid (HCl), phosphorous pentoxide (P₂O₅), or polyphosphoric acid (PPA).

Severity of oxidation determines the temperature susceptibility of the product, with air rectified products (mild oxidation) having similar properties to those of straight run vacuum distilled (paving) asphalt binders. For this reason air rectified asphalt binders and vacuum distilled residues are used either directly, or in blends to produce finished products that have the same end use specifications. Oxidized asphalts binders have significantly different temperature susceptibility values due to higher asphaltene contents and have substantially higher softening points for a given penetration value. The combination of these properties cannot be obtained by simple distillation, or air rectification. The rate at which the oxidation reaction occurs is affected by feedstock properties and the conditions in the blowing unit such as; viscosity or penetration of the feedstock, reactivity of the feedstock, temperature, air flow rate, degree of agitation, pressure, air to feed ratio, and whether or not a catalyst was employed.

2.6.2.4 Synthetic, Natural and Post-Consumer Polymers

Polymer modification may now be the more recognized method with polymers added to bitumen for an exhaustive number of reasons. Natural and synthetic polymers
have been used since the early 20th century to improve bitumen properties in an overall properties concept and is typically limited commercial availability and economics. Since the middle 1960s about as many polymers have been tried in bitumen as there are reasons for trying them:

- Natural Polymers (e.g. Lignin)
- Plastomers (e.g. polypropylene, polyethylene, ethylene vinyl acetate)
- Elastomers (e.g. natural rubber, synthetic rubber, polybutadiene, butyl rubber)
- Thermoplastic Elastomers (e.g. styrene-butadiene block copolymers, polyolefin blends, thermoplastic polyurethane)
- Ground Tire Rubber (e.g. reclaimed scrap tires)

Polymer additives generally range from 1% to typical levels of 3%, to as much as 7% for some applications. Of those listed, thermoplastic elastomers of styrene-butadiene copolymers account for largest use of polymers in bitumen modification. These products typically stiffen bitumen at high temperatures and make bitumen less brittle at low temperatures with their rubber characteristics giving bitumen the best blend of properties to address desired performance characteristics depending on end use.

GTR, which has been used regionally for approximately 30 years, can range from as little as 5% to as much as 20% of the total binder weight, again depending on the properties being targeted. Environmental efforts, previously discussed, to eliminate stockpiles of discarded tires have resulted in more widespread use of crumb rubber in asphaltic blends. In comparison to thermoplastic elastomers, GTR also consists primarily of styrene-butadiene copolymers. However due to vulcanization GTR is a thermoset elastomer opposed to a thermoplastic elastomer.
Modified asphalt binders using thermoplastic and thermoset polymers are not truly blends but dispersions. As these polymers do not typically melt at normal modified asphalt processing temperatures, the effect of thermoplastic elastomers, SBS, and thermoset elastomers, GTR on asphalt binders depends highly on proper dispersion and solubility in asphalt binders. When polymers dissolve, the first step is a slow swelling process called solvation. Linear and branched polymers dissolve in a second step, but network and cross linked polymers remain in a swollen condition. Dispersion and solvation are primarily responsible for the elastic nature imparted to asphalt from thermoplastic and thermoset elastomer polymer modification. This can be explained by an analogy presented by (Meynard 1981):

Hypothetically, if twenty parts rubber are combined with eighty parts cement using water as a solvent the resulting product would act as a cementitious mass filled with rubber particles, Figure 2.7. In this example, cement is representative of a normal continuous phase as the resulting end product displays characteristic of the cement, or major component of the dispersion. This is somewhat representative of asphalt modified with linear or low molecular weight polymers or waxes, e.g. oxidized poly(ethylene).
Combining the same twenty parts rubber with eighty parts cement exchanging water for xylenes, or using a solvent that would dissolve the rubber, the resulting product would act more as a rubbery network filled with cement particles, Figure 2.10. In this case, the rubber is representative of an inverse continuous phase as the resulting product displays characteristics of the rubber, or minor component in the dispersion. The inversion of phase depicted in Figure 2.8 is indicative of the elastic properties imparted to asphalt through polymer modification with relatively low loadings of networked and cross linked polymers.
Although other factors may affect the reaction between polymer and asphalt such as blending time (González et al. 2012), blending temperature (Navarro et al. 2007) and relative surface area (particle size, texture and dispersions) (West et al. 1998, Putman et al. 2006, Shen et al. 2009), compatibility between polymer and asphalt binder is important for the reaction to fully occur which improves the binder characteristics (Chehovits 1992, Buncher 1995, Brule 1996, Daly et al. 1997, Ariey et al. 2002, Artamendi et al. 2006). Compatibility is governed by the chemical composition of both the polymer and the asphalt. Compatibility is normally demonstrated when the polymer is blended with the asphalt binder and properties improve to a desired level and stabilized within a reasonable period of time at a reasonable temperature. Synthetic polymers are produced with consistent properties which can generally be selected and adjusted to design polymers with asphalt compatible characteristics. Additionally, most GTR produced from scrap tires today consists of a relatively homogeneous blend of different
rubber polymers making compatibility more of a matter of asphalt composition than GTR composition. In fact, asphalt chemical composition can vary greatly depending on crude source. Asphalt is composed of varying amounts of asphaltenes (solids), resins (polar aromatics) cyclics (non-polar aromatics) and saturates (aliphatic oils). During the polymer asphalt reaction, the aromatics are absorbed by the polymer (Gawel et al. 2006). If the crude source is low on aromatics, compatibility problems are likely because of insufficient aromatics for the polymer to absorb. There is also concern that if few aromatics remain, cold temperature flexibility will be severely decreased (Airey et al. 2003). Often extender oils may be added to provide the required aromatics.

2.7 Ground Tire Rubber Modified Asphalt Binders

Research on GTR modified asphalt binders over the last 50 years confirms a favorable impact of GTR modification. This can be confirmed by the fact that GTR ranks second among the most common asphalt polymer modifiers, just behind styrene-butadiene-styrene copolymers.

Modern use of GTR in asphalt pavements began in the early 1960s with a highly elastic GTR modified binder and aggregate topping developed by Charles McDonald, Materials Engineer for the City of Phoenix, Arizona, in the early 1960’s (McDonald 1975, Huffman 1980). McDonald’s work expanded into the application of large surface treatment projects along with other crack relief and open-graded surface courses. In this early work asphalt rubber was field blended at the hot-mix plant and used immediately due to the inherent instability of the product (Morris 1976, McDonald 1978). Developments by the City of Phoenix and subsequently the Arizona DOT led to the
initial growth of asphalt rubber (AR) applications, which included surface treatments, interlayers, and AR open-graded friction courses (AR-OGFC) (Huffman 1980).

During the two decades following McDonald’s invention, use of asphalt-rubber materials increased as they proved useful in various pavement maintenance functional applications to include asphalt concrete (Stephens 1974, Piggot 1979, Oliver 1976, Oliver 1977), low modulus stress absorbing membranes (SAM) and stress absorbing membrane interlayers (SAMI) (McDonald 1971, Olsen 1973, Way 1976, Morris 1976, Bethune 1978, Gonzales 1979, Scott 1979, Huffman 1980, Schnormeier 1980) and crack and joint sealers for flexible and rigid pavements (Bethune 1978, Huffman 1980). By far the greatest utilization was in pavement maintenance applications.

In 1989 interest in use of GTR in HMA was tweaked by the Florida Department of Transportation (FLDOT) who initiated a study conducted at the National Center for Asphalt Technology (NCAT), Auburn AL, in response to action by the Florida legislature in passing Senate Bill 1192 on Solid Waste Management (Roberts et.al. 1989). In Bill 1192 the FLDOT was instructed to develop the necessary changes in specifications and procedures, as warranted by research and demonstration project evaluations, to permit the inclusion of granulated tire rubbers in hot mix asphalt (HMA) as a standard practice. The bill also required that an evaluation of current research results and field practice be conducted and that the results be presented to the legislature and the Governor. This report is the result of a review of the current state-of-art plus the opinion of the project staff in areas where inferences were required. The NCAT report included results from the two major processes of the time for incorporating ambient ground, granulated tire rubber, GTR, into HMA: the wet process, Asphalt Rubber and the dry process, Plus-
Ride. A follow-up report was published by Choubane et al. presenting the ten year performance evaluation of the asphalt rubber surface mixes constructed for the NCAT study. (Choubane et al. 1999). Findings reported were that the wet processed asphalt rubber improved crack resistance of surface mixtures. Less rutting was observed in the GTR modified dense mixtures and no beneficial difference was observed with respect to skid resistance.

New York State Laws were amended in 1987 requiring investigation and report on the technical and financial implications of mandating addition of scrap tire rubber to paving materials used in New York State public works, as well as on the impact that such action would have on the scrap tire problem. In response to the amended law and concern with the environmental effects of disposing of used motor vehicle tires, the New York State Department of Transportation (NYDOT) commissioned a study in 1989 (Shook et al. 1989). The study concluded that GTR from scrap tires generated in New York State could be disposed of by utilizing them in highway paving applications, such as pavement resurfacing, at increased cost over conventional asphalt mixes. Indications were that an equal dollar benefit would not be generated by improved pavement performance, such as reduced maintenance and rehabilitation costs. From this study, two primary recommendations related to materials and applications were that the NYDOT provide funding to a selected group of local agencies for the trial use of rubber-modified asphalt mixes for resurfacing projects, continue to study the pilot construction projects included in this study, and use the results to develop and promulgate generic specifications, including appropriate modifications for mix design, construction control and quality assurance testing, for GTR modified asphalt mixes that utilize GTR as part of
the aggregate. In 1991 an investigation, with similar findings to the NYDOT study, was conducted by the Joint Highway Research Project Engineering Research Station at Purdue University (Kaya 1992).

During the period from 1989 to 1991, following FLDOTs lead in evaluation of rubber modified asphalt, a number of agencies constructed projects for GTR modified asphalt evaluations. In 1990 the Virginia Department of Transportation (VADOT) began construction of four test sections of GTR modified asphalt hot mix using the McDonald process and developmental wet processing method from Rouse Rubber, using fine ground GTR (Maupin 1996). Dense graded, gap graded surface mixes and a base mix were constructed. GTR modified asphalt performed as well as conventional mixes at a cost of 64 to 102 percent more that of conventional mixes.

In 1991 the Georgia Department of Transportation (GADOT) constructed a test section in Henry County just south of Atlanta consisting of GTR modified surface mixture containing 6 percent GTR using the McDonald process (Brown et al. 1997). In addition to the I-75 section, two contract sections of terminal blended GTR loaded at 16 percent, by weight of binder, were constructed. These projects were evaluated from 1991 to 1995, with the state indicating a preference to the terminal blend GTR as they felt the McDonald process did not allow time to test binder properties. GADOT also reported an increase to the cost of GTR modified HMA compared to conventional HMA at 50 to 100 percent increases, this was believed to be due to the cost of producing and placing the GTR modified HMA.

In 1991, Section §1038(d) of the Intermodal Surface Transportation Efficiency Act (ISTEA) required states to use a minimum amount of crumb rubber from recycled
tires in asphalt surfacing placed each year beginning with the 1994 paving season. The
ISTEA mandate caused a surge in interest in GTR technology prompting several
thorough literature reviews conducted on the subject within the four year period from
the FHWA conducted several two-day regional GTR workshops across the country in
1993 to provide government and industry a better understanding of the technology and
practices available at that time. Handout notes from these workshops provide excellent
and detailed review related to historical development, cost factors, crumb rubber modifier
technologies, production of crumb rubber, binder design and mixture design. (Brown
Chehovits and Hicks 1993).

In 1994, a catalog and software database was developed by the University of
Nevada-Reno under the National Cooperative Highway Research Program (NCHRP).
(McCarthy 1994). The database began with the bibliography developed by Dr. Jon Epps
as part of NCHRP Synthesis 198: Uses of Recycled Rubber Tires in Highways (Epps
1994). Synthesis 198 lists 232 publications which had appeared before December 31,
1993 with the catalog listing an additional 469 publications entered into the database up
to June 30, 1994. The university was to continue updating both the catalog and database
regularly, however, currency extended only to 1996 after which existing documents were
transferred to the Rubber Pavements Association (RPA) resulting in a database
containing up to 1000 publications making this the largest single source for literature on
GTR. Information is available through the RPA at www.rubberpavements.org.
The ISTEA mandate was lifted in 1995, under Section §205(b) of the NHS Designation Act, a significant number of GTR asphalt pavement sections were placed and national research was fostered. Many States discontinued use of GTR after the mandate was lifted. However, Agencies such as Florida, Texas, and Rhode Island continued their use of GTR. In 2005, the State of California Public Resource Code Section §42700-42703 legislated the use of GTR.

There are two primary methods of incorporating GTR into HMA that are generally referred to as the “wet” and the “dry” processes (Kandhal 1992, Buncher 1995). The wet process blends GTR with asphalt and allows a prescribed reaction time prior to mixing the GTR modified binder with aggregate. The dry process adds GTR directly to the HMA mixture during production, usually added directly to the aggregate prior to introducing the required asphalt binder. Growth in use of GTR modified asphalt pavements can be credited to successful construction of high performance asphalt pavements primarily using GTR modified asphalt binders produced via two versions of the “wet” process: “asphalt rubber,” (AR) commonly referred to as the “wet process” and “rubber modified asphalt” (RMA) also referred to as “terminal blend.”

AR production in the McDonald wet process, consists of blending from 15 to 22 % GTR by weight of binder, of a typical maximum size around 1.5 mm (15 mesh) with asphalt binder at temperatures ranging from 175 to 190°C (≈ 350 to 375°F) and allowing them to react for 30 to 60 minutes before introduction into the hot-mix mixture production process (McDonald 1975, McDonald 1978, Heitzman 1992, Chehovits 1993). This process is normally performed entirely at the HMA production plant using portable rubber mixing facilities.
The term “reaction” is used loosely here to describe the change in binder properties when GTR is added to asphalt. As previously discussed this change in properties is more physical, due to swelling of the rubber particles, than chemical, and depends on proper dispersion of rubber particles and solubility in the asphalt binder (Chehovits 1993). Fully reacted particles may swell as much as three to five times their original size (Green 1977). As the GTR particle swells the asphalt viscosity generally increases and stabilizes when the swelling nears a maximum. Changes in properties are not only a result of the GTR particles swelling, but also because the asphalt is giving up lighter oils through absorption by the rubber all in the process of phase inversion as discussed. Depending on temperature, GTR particle size, dispersion efficiency and shear, the reaction time with the McDonald process is typically 30 to 60 minutes. Improved dispersion and finer GTR particles may be used with the McDonald process to reduce reaction time and temperature. The time to fully react has been stated to be a direct function of the GTRs relative surface area prompting use of finely ground GTR (Lynch 1986, Rouse 1994, Rouse 1994, Lehigh 2015).

A significant drawback with the McDonald AR process is that it is a batch processing requiring special blending equipment to react the GTR with asphalt at elevated temperatures for a specific duration which can lead to delays at the hot-mix plant. Therefore, significant cost savings can be recognized by continuous blending processes or adding GTR to the mixture dry versus the wet process due to reduction in processing and materials handling (Bass 1992, Bloomquist 1993, Buncher 1995). Rouse Rubber Industries developed a non-proprietary continuous blending method called the Florida generic wet process, first used in Florida in 1989, using fine ground GTR that
eliminated the drawbacks of the McDonald batch process (Page et al. 1992, Page et al. 1993). In the dry process GTR may be brought to the job site in bulk or super-sacks, blown into a mineral filler silo, and fed into the drum by auger and belt similar to dry additives such as mineral filler. Another factor believed to drive the cost of AR higher than dry add GTR is the belief that, once blended, the AR has a shelf life limited to 24 hours (Chehovits 1993, Takallou 1992). This is primarily due to higher loadings of GTR used in the AR process, often upwards of 20%, and continued swelling of the rubber in mixtures stored at elevated temperature causing HMA producers alarm if an unexpected shutdown should occur at the production plant or jobsite. Stroup-Gardiner also reported that production of AR may be slower than the dry process with an average increase of 60% to dense graded mixture production compared to 20% increase with the dry process when equivalent GTR particle sizes were used (Stroup-Gardiner 1993).

The original dry process, known as PlusRide™, developed in Sweden in 1960 and licensed in the US in 1978, used 3% reduced sized rubber added directly into the heated aggregate prior to the addition of the binder. The PlusRide™ system used GTR of the “coarse” variety (by weight of mix) with a maximum particle size of 6.3 mm (3 mesh) and approximately 65% (by weight) larger than 2.0 mm (10 mesh) intended to replace a portion of the aggregate with coarse rubber particles to achieve a “flexible aggregate” effect.

Takallou introduced the first form of a generic dry add system, referred to as TAK™, in 1986 (Takallou 1987, Takallou 1988, Takallou 1992). The TAK™ system though similar to PlusRide™ differed in that it normally used 1 to 3% GTR (by weight of mix), slightly less than PlusRide™, and rather than using a fixed gradation the GTR
gradation was selected based on the aggregate gradation, adjusting the GTR gradation based on where the rubber particles could fit. GTR swelling was taken into consideration when selecting GTR gradation. Additionally, TAK™ incorporated a bimodal modification concept using a much finer particle size GTR in which half was selected of a size (greater than 10 mesh) designed to function as aggregate and the other half was selected of a size (less than 10 mesh) intended to modify the binder.

Though dry addition of GTR has had only limited past success, recent efforts have been employed to recycle GTR by dry addition in the hot-mix asphalt mixing process using additives and processing aids (Hines 2007, Clark 2014). These recent efforts, known as Asphalt Plus™, generally consist of adding 600 to 420µm (30 to 40 mesh) GTR, along with select additives, to mixtures in a similar manner as PlusRide™ with exception of utilization of considerably smaller rubber particles with the intention of binder modification in lieu of aggregate replacement. These additives are represented to provide an improved modified asphalt paving binder by incorporating a small amount of additive or processing aid into GTR modified asphalt binder which in turn leads to easier mixing, reduced tackiness, reduced cracking, less permanent deformation, lower life-cycle cost, and longer service life (Burns 1999).

As with similar dry processes from the late 1980s which incorporated finer rubber particles to partially modify the asphalt binder (Takallou 1987, Takallou 1988, Heitzman 1992, Buncher 1995), there is concern as to the function of the finer GTR particles. Do they actually react with the binder in the dry process as in the wet process or do they only partially react with the binder; or do they not react with the binder at all, rather acting as an inert filler. Mixture blending temperatures and times may be inadequate to achieve
the reaction with the binder necessary in thin films since wet processes occur at much higher blending temperatures. There are many variables associated with performance of GTR modified asphalt binders for production of hot-mix asphalt other than the process or technology used.

The alternative version to the AR wet process, RMA mentioned previously, is commonly referred to as “terminal blend” (Hicks et al. 2010). RMA or terminally blended GTR modified asphalt is produced in a similar manner to AR, except that production occurs in fixed blending facilities. RMA generally consists of blending GTR of a size range from 600µm to 177µm (30 to 80 mesh) with asphalt binder at temperatures ranging from 175 to 190°C (≈ 350 to 375°F) and allowing them to react for 60 (+) minutes prior to transfer to large storage tanks. Once mixed, the RMA is stored at elevated temperatures awaiting delivery to hot-mix production facilities in the same manner as conventional asphalt binders. Note that 600µm to 420µm (30 to 40 mesh) are more typical sizes for GTR in RMA, which is commonly referred to as 30 minus rubber.

Proprietary processes are available for production of RMA eliminating the need for on-site blending units while providing tank storable binders for HMA production. Early versions of these products FLEXOCHAPE and ECOFLEX allowed the asphalt binder to be blended at refineries or asphalt terminals like conventional ACs, without modification at the mix plant (Sainton 1989, Takallou 1992, Ecoflex 1993). Compared to AR at 20% loading of GTR these processes used only 10% loadings by weight of asphalt and were only used sparsely in the United States during the early 1990s (FHWA 1993). In the middle 1990s a number of U.S. patents were issued to Neste/Wright Asphalt Products Company of Channelview Texas, now referred to as the “Wright Process,”
involving RMA processes in which approximately 10% GTR was added to asphalt and processed at elevated temperature for extended periods to provide an asphalt rubber product that was storage stable for HMA production (Flanigan 1995, Flanigan 1996a, Flanigan 1996b). The advent of the Wright process has spawned development of a number of RMA processes, making terminal blend RMA one of the preferred processes for formulation of GTR modified binders for production of GTR modified HMA (Zanzotto 1996, Billiter et al. 1997). Some states now prefer terminal blended rubber, RMA, over AR even though AR has been the staple of their GTR modified pavements program (Kliewer 2015). Terminal produced RMA binders has also lead to production of hybrid binders of GTR combined with synthetic polymers as well as improvements in testing and certification of GTR modified asphalt binders (Abdelrahman 2006).

2.8 Properties and Specifications of Modified Asphalt Binders

GTR modified asphalt binders are generally less sensitive to temperature than conventional asphalt binders, thereby improving HMA performance (Chehovits 1989, Chehovits 1993). Higher relative stiffness at high operating temperatures is desired and is increased by addition and reaction of GTR, while desired lower relative stiffness at low operating temperatures is generally achieved by use of lower viscosity base asphalt cements or adding extender oils to soften the base binder. The base binder for modification with GTR in the AR and RMA processes is typically one or two grades lower than the standard binder used for HMA paving in a specific region. While stiffness is the primary measure of the difference between conventional asphalt and GTR modified asphalt, other empirical and physical properties have been evaluated, such as changes in
softening point, penetration, elasticity, flexibility, and ductility (Shuler et al. 1993, Buncher 1995). Generally, results show improved high temperature properties with added GTR. Low temperature improvements are not as prevalent but can be obtained with the combination of a softer binders and GTR concentration. Testing variance on GTR modified binders is often higher than on conventional binders, possibly due to inconsistent concentrations or improper mixing parameters of the GTR the binder.

Shuler et al. (1993) reported four principal tests evaluation of asphalt-rubber behavior including force-ductility, double-ball softening point, rotational viscosity, and size exclusion chromatography. Laboratory testing results indicated properties of field prepared AR could be duplicated in laboratory prepared blends. Condition surveys from three full-scale test pavements provided information on the most effective combinations of asphalt and tire rubber for interlayer construction. Rotational viscosity was used to simultaneously blend rubber and asphalt as well as monitor changes in consistency. The variation in consistency with increasing rubber content was presented as a possible means of monitoring rubber concentration during construction. AR viscosity was reported to increase with time and temperature. Chemical analysis of the asphalt and rubber blends by gel permeation chromatography further indicated that modification occurs to the asphalt as a function of blending temperature and time.

2.8.1 Purchase Specifications

Agencies specifying AR modified asphalt pavements tend to follow specifications based on their experiences. The format and extent of the specifications from different agencies may be different from each other, but generally they have common components
describing the type of product or process, materials including specification and test methods, construction requirements, methods of measurement and basis for payment.

Purchase specifications for asphalt binders primarily include test results to characterize the stiffness of asphalt binders with respect to expected end use conditions complimented by tests to ensure safety, consistency and retention of properties due to aging. Test methods and specifications for asphalt binders remained relatively unchanged for more than half a century, until the introduction of viscosity-based specifications in the late 1960s. Prior to the 1960s purchase specifications for asphalt binders were generally restricted to penetration graded binders. The penetration grading system, perhaps the oldest machine determined asphalt test, dates back to the late 1800s, with the development of the Bowen Penetration Machine (Halstead et al. 1974). In the early 1900s, use of the needle penetration test was adopted by ASTM in 1903 with the current version being adopted in 1959 (ASTM D-4, AASHTO T49). In the standard penetration test a container of asphalt, typically around 50 ounces, is brought to the standard test temperature, e.g. 25°C (77°F), in a thermostatically controlled water bath. The sample is placed under a needle of prescribed dimensions. The needle is loaded with a 100 gram weight and is allowed to penetrate the asphalt cement for five seconds. The depth of penetration is measured in units of 0.1 mm (dmm) and is reported as penetration units (Brown et al. 2009). Penetration grading’s basic assumption is that the less viscous the asphalt, the deeper the needle will penetrate. Penetration depth was roughly empirically correlated with asphalt binder performance. Asphalt binders with high penetration numbers, soft binders, were used for cold climates while asphalt binders with
low penetration numbers, hard binders, were used for warm climates. Penetration grade specifications according to AASHTO M20 and ASTM D 946 are presented in Table 2.3.

Table 2.3
AASHTO M20 and ASTM D 946 Penetration Graded Asphalt Binders

<table>
<thead>
<tr>
<th>Penetration Grade</th>
<th>40 - 50</th>
<th>60 - 70</th>
<th>85 - 100</th>
<th>120 - 150</th>
<th>200 - 300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration at 77°F (25°C) 100g, 5s, dmm</td>
<td>Min</td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>Flash Point °F</td>
<td>450</td>
<td>***</td>
<td>450</td>
<td>***</td>
<td>450</td>
</tr>
<tr>
<td>Solubility in Trichloroethylene, %</td>
<td>99.0</td>
<td>***</td>
<td>99.0</td>
<td>***</td>
<td>99.0</td>
</tr>
<tr>
<td>Retained Penetration after TFO, %</td>
<td>55+</td>
<td>***</td>
<td>52+</td>
<td>***</td>
<td>47+</td>
</tr>
<tr>
<td>Ductility at 77°F (25°C) after TFO, cm</td>
<td>***</td>
<td>***</td>
<td>50</td>
<td>***</td>
<td>75</td>
</tr>
</tbody>
</table>

Penetration specifications were supplemented and for the most part eventually replaced by the introduction of and improved asphalt grading system based on viscosity in the early 1960s. A rational scientific viscosity test replaced the empirical penetration test as the key parameter for asphalt binder characterization. Viscosity grading may be performed on both original as-delivered asphalt binder or on aged residue (AR) samples. Original asphalt binder, asphalt cement (AC), viscosity grading is referred to as AC grading with asphalt binder grading on aged residue samples being referred to as AR grading. AR viscosity testing is performed on aged residue from the rolling thin film oven test. AC grading of asphalt binders is characterized by properties the AC exhibits.
before the HMA manufacturing process while AR grading attempts to simulated asphalt binder properties after the HMA manufacturing process to be more representative of binder performance in HMA pavements. With both the AC grading system and the AR grading system, absolute viscosity (ASTM D2171, AASHTO T202) is measured at 60°C (140°F) and is reported in poise or centimeter gram seconds (cm-g-s) or dyne second per centimeter squared (dyne-s/cm²), named after Jean Louis Marie Poiseuille (“Jean-Louis-Marie Poiseuille” 2015). Table 2.4 shows standard viscosity grades for the AC and AR grading systems form AASHTO M226 and ASTM D3381. Lower viscosity values, lower poises, indicate lower viscosity and thus the asphalt cement flows more readily. For example, an AC-5 (specification viscosity is 500 ± 100 poise at 60°C (140°F)) is less viscous than AC-40 (specification viscosity is 4000 ± 800 poise at 60°C (140°F)). Typical grades used for HMA paving in the U.S. are AC-10, AC-20, AC-30, AR-4000 and AR 8000.

Table 2.4

<table>
<thead>
<tr>
<th>Standard</th>
<th>Original Asphalt (AC) Grading</th>
<th>Aged Residue (AR) Grading</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D 3381</td>
<td>AC-2.5, AC-5, AC-10, AC-20, AC-30, AC-40</td>
<td>AR1000, AR2000, AR4000, AR8000, AR16000</td>
</tr>
</tbody>
</table>

Since GTR modified asphalt binders are non-homogeneous, dispersed rubber particles tend to confound characterization by penetration and absolute viscosity; therefore, non-standard procedures have been used to attempt to quantify the modified physical properties of AR binders. (Chehovits 1989) reported early non-standard tests to include: Schweyer rheometry, sliding plate viscosity, force ductility, torque fork
viscosity, and mechanical spectography. Common physical attributes of AR rubber under consideration for hot-mix applications included viscosity at high temperature to ensure mixing and compaction characteristics, consistency at high temperatures and moderate temperatures to address properties at pavement surface temperatures, elasticity and low temperature characteristics.

Viscosity of AR materials at high temperature \( \approx 120-200^\circ C \) (250-400°F) has typically been monitored using rotational type viscometers, more typically Haake hand held portable viscometers or Brookfield (ASTM D3236) viscometers. Portable viscometers facilitate field viscosity measurements during the AR blending process.

High temperature consistency at temperature representative of high pavement surface temperatures has commonly been evaluated using several procedures the more common being the Ring and Ball Softening Point (ASTM D36).

Additional tests for high temperature consistency included a Modified Flow, or a cone penetration at 50°C (122°F) (ASTM D3407, ASTM D5). Moderate temperature, e.g. 25°C (77°F) and low temperature e.g. 4°C (39.2°F) properties can also be easily evaluated using the cone penetration test. A modified version of the cone penetration test also allowed for simple evaluation of elasticity indicated by the amount of rebound under a 75 gram load at 25°C (77°F).

Low temperature properties have been characterized by ductility at 4°C (39.2°F) (ASTM D113) and a modified low temperature flexibility test in accordance with ASTM D711.

According to ASTM, AR is a blend of asphalt cement, reclaimed tire rubber, and certain additives in which the rubber component is at least 15% by weight of the total
blend and has reacted in the hot asphalt cement sufficiently to cause swelling of the rubber particles (ASTM D8-97). ASTM further defines the detailed requirement on base asphalt cement, ground recycled tire rubber, and three types of asphalt rubber binders: Type I recommended for use in hot climates; Type II recommended for use in warm climates; and Type III recommended for cold regions (ASTM D6114-97(2002)). The more common tests specified for AR binders are field blend rotational viscosity, softening point, cone penetration, and resilience. Table 2.5 presents typical AR specification requirements obtained from various agencies (Hicks 2012).

Table 2.5
Asphalt Rubber Specification Parameters from Various Agencies

<table>
<thead>
<tr>
<th>GTR Loading (min) %</th>
<th>Blending Temperature °C (°F)</th>
<th>Blending Time (min) Minutes</th>
<th>Viscosity cps (min-max)</th>
<th>Softening Point (min) °C (°F)</th>
<th>Cone Penetration dmm</th>
<th>Resilience (min) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 - 22</td>
<td>(165 – 226)</td>
<td>30 - 60</td>
<td>1500 - 5000</td>
<td>52 - 74</td>
<td>10 - 100</td>
<td>10 - 25</td>
</tr>
</tbody>
</table>

2.8.2 Performance Specifications

Strategic Highway Research Program (SHRP) research had a significant impact on characterization and specification of asphalt binders through development more fundamental rheology based test methods, advances in instrumentation and advanced capabilities of personal computers permitted routine application of rheological methods for use in conducting and determining specification compliance. As a result of SHRP the 1990’s saw the introduction a new binder purchase specification now known as the Superpave binder specification. The Superpave binder specification is based on rheological properties of the asphalt binder measured over a wide range of temperatures.
and aging conditions. Various pieces of equipment are used to measure stress strain relationships in the binder at the specified test temperatures. This equipment includes the Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR). Measuring binders' rheological properties over a wide range of temperatures, loading conditions, and aging conditions allows performance relationships to be established between the test results and the pavement. The details of this asphalt binder testing are described in the American Association State Highway and Transportation Officials AASHTO Specification (AASHTO) M 320.

The advent of the Superpave binder specification encouraged wider use of terminal blend GTR modified asphalt binders, RMA. RMA binders, used since the early 1900s, are similar to polymer modified asphalt and can be used in any hot mix or surface treatment application where polymer modified asphalts are used. Unlike AR modified binders, RMA is stable without the need of agitation during storage or transportation. Depending on specifications, RMA contains 5-20% GTR by weight of asphalt and can be used just like conventional liquid asphalt cement.

While conventional binder classification specification may be used with RMA, as with AR, the non-homogeneous nature of RMA may also confound results of conventional binder specification testing (Reese 1994). Only minor adjustments may be needed to facilitate Superpave binder testing of RMA binders using GTR particles less than 30 mesh, such as increasing the standard DSR plate-plate testing gap from 1 mm to 2 mm. Additionally, for larger particles greater than 30 mesh alternative testing fixtures are available to provide rheological testing of a wider gap nature to as much 4 mm. Rheology testing of RMA binders whether with standard 1 mm gap, increased gap or
with alternative geometries allows adherence to standard Superpave binder grade parameters including recent modifications to the specification such as multiple-stress creep and recovery (MSCR).

2.9 Asphalt Mixture Performance

Polymer modified asphalt (PMA) binders are widely used in HMA to meet the demands of today’s high traffic loadings. Improvements in resistance to permanent deformation (rutting), fatigue cracking and thermal cracking are sought for the life of the pavement. GTR modified asphalt has rapidly become accepted to meet these demands (Maccarrone et al. 1995).

Of important note, (Buncher 1995) reported rubber industry claims of improvement in almost all aspects of mix performance through use of GTR modified asphalt. As a caution to the reader, a clear bias was expressed when publications were compared that had been written by rubber producers versus independent authors. Not that claims presented were untrue, just a caution that one should be aware of an author’s background, this precaution holds is also advisable in the present as many claims remain to be based on mere speculation.

During the early to late 1990s studies were conducted by a number of agencies utilizing various GTR modification methods. Similar findings were reported by Alaska (Saboundjian et al. 1997), Arizona (Way 1999, Kaloush et al. 2002), South Carolina (Amirkanian 2001), Louisiana (Huang et al. 2002), California (Shatnawi 2007) and Colorado (Shuler 2011). A common theme was improved binder properties of GTR modified asphalt binders and improved mixture performance.
One such improvement was greater resistance to permanent deformation realized due to improvements in high temperature binder stiffness through GTR modification and the subsequent increase in mixture stiffness. This result was not unexpected as the relationship between binder and mixture stiffness has been well documented by Van der Poel and later verified and improved upon by Heukelom and Klomp. This binder and mixture stiffness relationship is key to a number of predictive relationships developed to estimate the stiffness and dynamic modulus of mixtures from simpler material properties (Brown et al. 2009). However, studies have shown rutting to be more a function of the mineral aggregate character (angularity and gradation) and the percentage of voids filled with binder, rather than of binder stiffness (Cross et al. 1992, Kandhal et al. 1990).

Unlike the nomographs of Van der Poel, Huekelom and Klomp, in consideration of the mixture designs role in resistance to permanent deformation, later predictive models include contributive inputs from mixture components to include gradation data, air voids and effective asphalt content in addition to binder stiffness inputs (Bari et al. 2006).

The optimum binder content is generally higher when using AR which can result in better aging properties due to thicker binder films. Conversely, lower lab mix stability has been reported when using AR versus a conventional AC (Heitzman 1992, Chehovits 1993, Kandhal 1993, Buncher 1995) contesting the claims that mixtures produced with AR reduce deformation potential by increasing mix stability, if not for the field performance results reported. Antioxidants and carbon black from the tire rubber compound are also believed to reduce aging. Combined with higher optimum binder content and thicker films greater mix durability in resistance to fatigue and thermal cracking is expected as a result of GTR modified asphalt binders.
Claims have been made to the ability of GTR modified asphalt binders to reduce fatigue cracking in HMA (Buncher 1995). Addition of GTR is said to increase the elasticity of the binder thereby in allowing the mix to better resist the repeated tensile stresses caused from repeated wheel loads. (Raad et al. 1993) reported HMA produced with AR binder withstanding 5 to 20 times more load repetitions than conventional HMA before failure. In a follow-up study, Raad et al. (1998) reported findings of laboratory and field investigations sponsored by the Alaska Department of Transportation (AKDOT). Fatigue relationships were developed in terms of repeated flexure strain, dynamic flexure stiffness of the mix, and repetitions to failure. Relationships for the dynamic flexure stiffness as a function of temperature were also developed. Dissipated energy associated with repeated flexure stress and strain was determined and used to assess the damage behavior of conventional and rubberized mixes. The proposed fatigue equations were then used to compare the behavior of the rubberized mixes with conventional mixes. Results of these investigations indicated improved fatigue performance of the GTR modified HMA sections in comparison to conventional HMA pavements. These results were also confirmed by a field aging study on fatigue performance of conventional HMA and AR HMA involving conventional dense-graded mixture (CAC-DG) and asphalt-rubber hot mix gap-graded (ARHM-GG) in California (Raad et al. 2001).

Reduced thermal cracking of HMA constructed with GTR modified asphalt binder is believed to be a result of the GTR modified binder being more flexible, less stiff, under low temperature performance conditions. In contrast to the previous discussion of the relationship of binder stiffness as the primary contributing factor to
resistance to permanent deformation, (Buncher 1995) cites an informal reference to estimations that thermal cracking is influenced more than 88% by binder alone and less than 12% by other mix properties. This is acceptable as it is commonly believed by HMA researchers that binder alone influences cracking in asphalt mixtures from 80 to 90% while other properties only have a 10 to 20% impact, however, this may not consider the effect binder-aggregate adhesion may to cracking in some mixtures.

Polymer modification of asphalt binders provides some improvement to low temperature properties, low temperature performance is believed to be primarily attributed to base binder properties rather than polymer contributions (Morrison et al. 1995). Recall from the discussion of why we modify asphalt that softer grade binders generally selected as the base for modification thereby achieving high temperature stiffness from modification and low temperature flexibility from the base binder. If the base binder exhibits good temperature susceptibility and retains low temperature properties throughout the pavements life this should provide for the majority of improvement in low temperature HMA performance allowing better resistance to thermally induced tensile strains (Lenoble et al. 1994). In a performance evaluation of Arizona AR, Kaloush et al. (2002) reported AR mixes to show superior performance compared to standard asphalt concrete mixtures when resistance to thermal cracking is considered. The results of strain at failure showed that the AR mixes mixtures had higher strain values than conventional mixture. Asphalt rubber mixtures with higher strain at failure showed higher resistance to thermal cracking. Of important note, Kaloush et al. (2002) also reported, with AR mixtures, strain at failure and energy parameter from the same test provided better indication of the field behavior of the mixes than the indirect
tensile strength test parameter providing better indication of the field behavior of mixtures.

Mixtures containing GTR modified asphalt binders are expected to experience less reflective cracking from underlying pavement crack movement than conventional HMA mixtures. GTR modified asphalt binders are believed to be more elastic than conventional asphalt cement thereby withstanding greater strain before failure (Caltabiano et al. 1991).

2.9.1 Mixture Considerations

Standard mix design procedures, Marshall, Hveem and Superpave, have been used to design mixtures containing AR and RMA. As previously stated, addition of GTR, specifically AR, may raise optimum binder content and lower laboratory stability results in dense graded mixtures regardless of mix design methodology, this may not hold true with RMA depending on GTR loading. This increase in optimum binder content is generally due to higher viscosity of AR and RMA compared to conventional AC which prevents close packing of aggregate, therefore, requiring more binder to achieve the same voids in total mixture (VTM) (air voids), thereby resulting in decreased laboratory measured stability.

High loadings of GTR and coarse rubber particles involved when using AR, the aggregate selected will often have higher voids in the mineral aggregate (VMA). Increased VMA due to opening of the gradation of dense-graded mixtures containing AR makes room for swelled GTR particles. Recalling that rubber particles may swell as much as 7 times their original size, if these soft swollen particles bridge aggregate-
aggregate interaction, compaction may be an issue (Kandhal et al. 1993, Chehovits et al. 1993, Celik et al. 2008). This is less of an issue with RMA containing lower loadings of smaller particle size GTR; however, it may be an issue depending on degree of reaction of the GTR particles and AC.

Open-graded friction course (OGFC) and stone matrix asphalt (SMA) with AR and RMA can be designed with standard methods as both typically require higher optimum binder contents compared to dense-graded mixtures. Increased optimum binder content required with open and gap-graded mixtures may lead to issues with “drain down” of the hot AC from the aggregate after mixing unless a binder stabilizing agent such as cellulose fibers is used. Additionally, higher viscosity provided by GTR modified asphalt binder serves to lessen issues with drain down due to thicker films.

2.9.2 Pre-Blended Rubber and Binder vs Dry Mixture Addition

Earlier versions of dry mixture addition of GTR to asphalt mixtures posed more of an issue than dry mixture addition processes currently employed. Early dry mixture addition concepts, PlusRide™ and TAK, were typically intended to rubberize the aggregate rather than modify the asphalt binder. These systems were collectively referred to as Rubber Modified HMA (RUMAC) by (Buncher 1995). RUMAC systems typically used GTR particles of 10 mesh or greater at a common mixture loading of 3%. The TAK system attempted to modify both mixture and binder by using 1 to 3% of a combination of GTR particles larger than 10 mesh and less than 10 mesh with the larger particles believed to be an aggregate modifier and the smaller particles believed to modify the binder.
GTR loadings of 3% in the mixture would be equivalent to 37.5% of a binder loading of 5% if the added GTR acts as a binder modifier. As a general rule binder contents in the dry addition processes were increased by as much as 2% additional binder. Even at the increased binder content GTR loadings of 1 to 3% is equivalent to 12.5 to 30% binder modification if the added GTR acts as a binder modifier.

A precursor to current dry mixture addition processes, possibly derived from the TAK system, referred to by Buncher (1995) as the “new generic dry” addition system used smaller GTR particles of from 16 to 80 mesh at loadings of less than 1.5% by weight of mixture. Smaller GTR particles were intended to modify the asphalt binder rather that modify the mixture. GTR loadings of 1.5% by weight of mixture in mixtures with 5% binder content would be equivalent to binder modified with 23% GTR. (Buncher 1995) reported the new generic dry addition system to be used by four states (Arkansas, Iowa, Kansas and Oklahoma) with only one (Kansas) using the concept successfully for an extended period. The use of ultra-fine particle (80 mesh) GTR is attributed to the improved performance of the new generic dry concept in Kansas.

The accepted version of dry mixture addition used today is a modified version of the new generic dry system with the exception of larger particle sizes of the 30 to 40 mesh range, often referred to as minus 30 rubber. GTR loadings are also considerably less as they are considered to be approximately 10% of the added binder which equates to approximately 0.5% of the total mixture mass. Today’s dry mixture addition methods, also known as belt add modifier (BAM), often contain additional additives such as polymers or waxes to provide improved mixing and compaction characteristics. These
additives are believed to do more in improving mixing and compaction than actually function as a property modifier of the base AC.

Of primary concern with dry mixture addition or BAM is whether there is sufficient time in the HMA mixing process to allow for expected binder modification (Lougheed et al. 1996, Moreno et al. 2011). Moreno et al. (2011) suggests that the optimum GTR content and digestion time for dry mixture addition was 1% and 90 minutes respectively. This would equate to a GTR loading of from 16 to 20% based on the binder contents used in the study.
CHAPTER 3
MATERIALS TESTED

3.1 Overview of Materials Tested

A total of forty-eight bituminous combinations were tested throughout this work consisting of nine base asphalt cements and thirty-six modified binders. Modified binders were prepared from asphalt cements taken from by eight different suppliers. An accounting of the bituminous combinations tested along with and explanation of rational for asphalt selection is presented in this chapter. Descriptive identification of each asphalt cement as well as modified binders prepared there from are given.

GTR, reclaimed from whole tire recycling, was supplied by Polyvulc USA, Inc., Vicksburg, Mississippi and Winnsboro Rubber Recycling, Winnsboro, Louisiana. Other polymer additives, SBS and Trans-polyoctenamer (TOR), were Vector 2411 supplied by Dexco Polymers, Houston, Texas and Vestenamer 8012 supplied by Evonik Industries (Degussa), Parsippany, New Jersey.

Twenty-Five rubber compounds were tested, sixteen of which were compounded and supplied by Smithers Rapra North America of Akron Ohio. The remaining nine were random sampled 30/40 mesh from various GTR suppliers.

Granite aggregates from Rinker Materials Aggregate Division and mix designs for comparative mixture evaluations were supplied by The Scruggs Company, Hahira,
Georgia. Limestone aggregates from Mathy Construction and the E1 mix design for mixture performance verification were supplied by Mathy Technology and Engineering, Onalaska, Wisconsin.

3.2 Asphalt Cements and Binders

Forty-Eight bituminous combinations were tested throughout this work and are grouped as follows according to the specific chapter of this dissertation.

Nine asphalt cements (implying no modification; only bituminous material) were used as neat PG binders (binder is a term that implies a material may or may not contain more than bituminous material) and as base asphalts for binder modification and mixture evaluation in this work. They were:

1. Lion Oil Company (LO) – PG 64-22 from the Lion Oil Company refinery in El Dorado, Arkansas;
2. ExxonMobil (EM) – PG 64-22 from the ExxonMobil refinery in Billings, Montana;
3. San Joaquin Refining (SJR) – AR 4000 from the San Joaquin refinery in Oildale, California;
4. Shell Oil Company (SO) – AR 4000 from the Shell Oil refinery in Martinez, California;
5. Nynas (NS) - 50-70 dmm (penetration graded) from the Nynashamn refinery in Nynashamn, Sweden;
6. Total Brenstar (TB) – 50-70 dmm (penetration graded) from the Total refinery in France;
7. Orlen (OP) – 50-70 dmm (penetration graded) from the Polski Koncern Naftowy Orlen (PKN) refinery in Plock, Poland;


LO PG 64-22, asphalt cement number 1, was the primary base asphalt utilized for the work encompassed by Chapter 6, consisting of the following modified binders:

10. 5.0% GTR in LO PG 64-22 (herein after referred to as LO 5.0% GTR);

11. 7.5% GTR in LO PG 64-22 (herein after referred to as LO 7.5% GTR);

12. 10.0% GTR in LO PG 64-22 (herein after referred to as LO 10.0% GTR);

13. 5.0% 20 mesh GTR plus addition of trans-polyoctenamer (TOR) at 4.5% by weight of GTR loading in LO PG 64-22 (herein after referred to as LO 5.0% GTR/TOR);

14. 7.5% 20 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in LO PG 64-22 (herein after referred to as LO 7.5% GTR/TOR);

15. 10.0% 20 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in LO PG 64-22 (herein after referred to as LO 10.0% GTR/TOR);

16. 10.0% 20 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in LO PG 64-22, plus post addition of 1% elemental sulfur;

17. 10.0% 20 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in LO PG 64-22, processed at 210°C (410°F);
18. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in LO PG 64-22, processed at 210°C (410°F);

19. 10.0% 60 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in LO PG 64-22, processed at 210°C (410°F).

Six additional GTR/TOR modified binders were prepared for Phase IV of Chapter 6 utilizing asphalt cements 2 – 6, these binders are described as follows:

20. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in EM PG 64-22 (asphalt cement number 2) processed at 410°F, herein after referred to as EM GTR/TOR;

21. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in SJR AR 4000 (asphalt cement number 3) processed at 410°F, herein after referred to as SJR GTR/TOR;

22. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in SO AR 4000 (asphalt cement number 4) processed at 410°F, herein after referred to as SO GTR/TOR;

23. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in NS 50-70 dmm (asphalt cement number 5) processed at 410°F, herein after referred to as NS GTR/TOR;

24. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in TB 50-70 dmm (asphalt cement number 6) processed at 410°F, herein after referred to as TB GTR/TOR;
25. 10.0% 40 mesh GTR plus addition of TOR at 4.5% by weight of GTR loading in OP 50-70 dmm (asphalt cement number 7) processed at 410°F, herein after referred to as OP GTR/TOR.

LO PG 64-22 was also used as the base binder for initial testing used in specification development work of Chapter 7. Additional binders to neat LO PG 64-22 included:

26. PG 70-22 – LO PG64-22 plus PPA;
27. PG 76-22 – PG70-22 (binder 24) plus 2.25% SBS;
28. LO PG 64-22 plus 10% 60 mesh GTR;
29. LO PG 64-22 plus 15% 60 mesh GTR;
30. LO PG 64-22 plus 10% 30 mesh GTR;
31. LO PG 64-22 plus 15% 30 mesh GTR;
32. LO PG 64-22 plus 15% 20 mesh GTR;
33. LO PG 64-22 plus 20% 20 mesh GTR;
34. LO PG 64-22 plus 11% 80 mesh GTR;
35. PG 64-34.

Binders in Chapter 8 are separated into two groups, according specific objectives, based on two CPW base asphalt cements of grades PG 67-22 and PG 64-22, asphalt cements numbers 8 and 9. Group I binders, 36 thru 39, are based on CPW PG 67-22 and were utilized in mixture comparison work of Chapter 8.

36. Neat CPW origin PG 67-22 (referred to as CPW PG 67-22);CPW PG 67-22 modified with pre-blended SBS polymer (propriety blend) to produce PG 76-22 binder (referred to as Ergon Asphalt and Emulsions (EAE) PG 76-22);
37. CPW PG 67-22 with dry added GTR/TOR (referred to as GTR Dry);
38. CPW PG 67-22 with wet pre-blended GTR/TOR modified binder that was lab produced to represent terminal blend crumb rubber and has formulation shown in Table 3.6 (referred to as GTR Wet).

Chapter 8 Group II binders, binders 40 thru 47, are based on CPW PG 64-22 and were utilized in DGA mixture performance verification of binders from specification development work discussed in Chapter 7.

39. CPW origin PG 64-22 modified with sufficient 20 minus GTR to produce a PG 76-22 binder (referred to as 20 Mesh hereafter);
40. CPW origin PG 64-22 modified with sufficient 30 minus GTR to produce a PG 76-22 binder (referred to as 30 Mesh hereafter);
41. CPW origin PG 64-22 modified with sufficient 60 minus GTR to produce a PG 76-22 binder (referred to as 60 Mesh hereafter);
42. CPW Origin PG 64-22 modified with sufficient 80 minus GTR to produce a PG 76-22 binder (referred to as 80 Mesh hereafter);
43. CPW origin PG 64-22 modified with 5% 30 minus GTR (referred to as 5% GTR hereafter);
44. CPW origin PG 64-22 modified with 10% 30 minus GTR (referred to as 10% GTR hereafter). This binder was also tested as a PG 76-22;
45. CPW origin PG 64-22 modified with 15% 30 minus GTR (referred to as 15% GTR hereafter);
46. CPW origin PG 64-22 modified with 20% 30 minus GTR (referred to as 20% GTR hereafter).
An additional Group II Hybrid binder, binder 47, was prepared with CPW PG 67-22, asphalt cement number 8, for subsequent DGA mixture verification testing presented in Chapter 8.

47. CPW origin PG 67-22 with SBS polymer and GTR (proprietary blend) to produce a PG 76-22 binder (referred to as Hybrid hereafter).

3.2.1 Asphalt Cement Selection

Asphalt properties and quality are dependent of crude oil source from which the asphalt is derived. Therefore, selection of asphalt used in this work was made using a Petroleum Administration for Defense Districts (PADDs) selection logic in order to somewhat evaluate effects of varying asphalt sources.

The Petroleum Administration for War (PAW), established through executive order in 1942, divided the United States into five districts for the purpose of allocation of fuels derived from petroleum products during World War II (WWII). While the PAW was abolished shortly after WWII, congress later passed the Defense Production Act of 1950 which created the Petroleum Administration for Defense (PAD). PAD adopted the same districts established by PAW referring to them as Petroleum Administration for Defense Districts or PADDs. While designed for war time administration, the PADD concept is used today for data collection purposes and to aid in understanding of supply and demand of the domestic petroleum products, including asphalt. Issues such as the Keystone pipeline, Bakken oil developments, West Texas Intermediate (WTI) price volatility, refinery closures, and natural disaster impacts can all be rationalized with an understanding of PADD basics. Figure 3.1 shows the current PADD delineation.
It is well understood that crude oil sourcing for U.S. refineries varies over time, but in general it can be assumed that, PADD 1 refineries process crude oil shipped from all over the world, primarily Venezuela during the period of this work. PADD 2 and PADD 4 depend primarily on crude oil produced and moved by pipeline from Canada supplemented by crude from PADD 3 as well as production from Rocky Mountain state sources. PADD 3 is the largest refining region and obtains crude oil from the Gulf Coast outer continental shelf, Mexico, Venezuela, and the rest of the world. Currently, permitting issues stalling construction of the Keystone pipeline is forcing rail transport of Canadian syncrude (from oil sands) to PADD 3 refineries. PADD 5 obtains crude oil primarily from Alaska (by tanker) and California (Kern River Valley), and through
imports. These assumptions were the basis of the logic used in selection of asphalt cements used in this work in order to ensure varied asphalt composition and properties.

Lion Oil Company (Eldorado, Arkansas) LO PG 64-22 from PADD 3, which was refined primarily from Saudi light crude oil when initially sampled for this dissertation, was selected as the base asphalt cement studying the effect of GTR modification, Chapter 6. LO PG 64-22 was selected as it was commonly used in the formulation of various PMA binders and has what is considered to be relatively good compatibility characteristics with common polymer modifiers.

In addition to the LO PG 64-22 asphalt, six asphalt cements from other sources were selected to evaluate the effect of asphalt source on GTR modified asphalt binder properties in Chapter 6. Asphalt cements selected from US sources were: one (1) from PADD 4, and two (2) from PADD 5. Two (2) asphalt cements were selected from PADD 5 in order to incorporate the distinct differences between asphalts from the California Valley, SJR PG 64-4, crude and other crude sources for California asphalts, SO PG 64-16. Three (3) asphalt cements were also selected from sources outside of the US: Nynas 50-70 dmm from Sweden, designated NS PG 64-22, (Derived from Venezuelan crude source comparable to asphalt cement from PADD 1 in the US market.) in the 2007 time frame; Total 50-70 dmm from France, designated TB PG 64-22, (Derived from North Sea crude source also comparable to PADD 1 as well as PADD 3 in the US market); and Orlen 50-70 dmm from Poland, designated OP PG 64-22, (Derived from Russian crude source thought to be partially modified by air blowing, which is also known as air rectified bitumen). Table 3.1 lists the asphalt cements selected, additionally, also listed are two asphalt cements not discussed above which will be discussed later in this section.
Table 3.1
Asphalt Cements Selected

<table>
<thead>
<tr>
<th>Asphalt Cement</th>
<th>Grade</th>
<th>ID</th>
<th>Supplier Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lion Oil Company</td>
<td>PG 64-22</td>
<td>LO</td>
<td>El Dorado, Arkansas</td>
</tr>
<tr>
<td>2. Exxon Mobil</td>
<td>PG 64-16</td>
<td>EM</td>
<td>Billings, Montana</td>
</tr>
<tr>
<td>3. San Joaquin</td>
<td>AR 4000</td>
<td>SJR</td>
<td>Bakersfield, California</td>
</tr>
<tr>
<td>4. Shell</td>
<td>AR 4000</td>
<td>SO</td>
<td>Martinez, California</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>50-70 dmm</td>
<td>NS</td>
<td>Sweden</td>
</tr>
<tr>
<td>6. Total</td>
<td>50-70 dmm</td>
<td>TB</td>
<td>France</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>50-70 dmm</td>
<td>OP</td>
<td>Poland</td>
</tr>
<tr>
<td>9. Conoco/Phillips</td>
<td>PG 64-22</td>
<td>CP</td>
<td>Wood River, Illinois</td>
</tr>
</tbody>
</table>

Note: Numbers 1 to 9 denote section 3.2 asphalt cement ID.

LO PG 64-22 was also used as the base asphalt cement for testing used in the specification development work of Chapter 7. For this work, eleven binders were evaluated: neat LO PG 64-22 and binders 24-33. Performance grading test results for these binders is discussed in Chapter 7.

While Lion Oil asphalt was a good choice at the beginning of this work, unexpected changes in crude source and refining processes at the Lion Oil refinery affecting the properties of LO PG 64-22 and prompted a change to asphalt cements supplied by Conoco Phillips, Wood River, Illinois (CPW) for work in Chapter 8; therefore, Conoco/Phillips Wood River (PADD 2) CPW PG 67-22 was selected for Group I binders of Chapter 8. CPW PG 67-22 was selected as it had similar polymer compatibility characteristics to the original LO PG 64-22 and met specification requirements of the Georgia Department of Transportation (GADOT) for the mixtures evaluated. This binder was used as the base binder for polymer modification as well as for GTR modification in the different mixture types compared in Chapter 8.
CPW PG 64-22, asphalt cement number 9, was selected to replace LO PG 64-22, asphalt cement number 1, as the base asphalt cement for all polymer and GTR modification for the Group II binders used in DGA mixture performance evaluations as a verification of binder specification work presented in Chapter 7.

### 3.2.2 Asphalt Cement Grading

Neat asphalt cements from Table 3.1 were graded in accordance with AASHTO M320 Standard Specification for Performance-Graded Asphalt Binders, results of asphalt cements 1 thru 9 are presented in Tables 3.2 through 3.5.

**Table 3.2**

<table>
<thead>
<tr>
<th>Asphalt Cement</th>
<th>Original Viscosity 135°C</th>
<th>Original G*/sinδ 64°C</th>
<th>Original G*/sinδ 70°C</th>
<th>Original P/F</th>
<th>RTFO Aged G*/sinδ 64°C</th>
<th>RTFO Aged G*/sinδ 70°C</th>
<th>RTFO Aged P/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lion Oil</td>
<td>456</td>
<td>1.310</td>
<td>0.655</td>
<td>66.3</td>
<td>2.472</td>
<td>1.211</td>
<td>65.0</td>
</tr>
<tr>
<td>2. Exxon Mobil</td>
<td>442</td>
<td>1.376</td>
<td>0.673</td>
<td>66.7</td>
<td>3.225</td>
<td>1.527</td>
<td>67.1</td>
</tr>
<tr>
<td>3. San Joaquin</td>
<td>254</td>
<td>1.299</td>
<td>0.551</td>
<td>65.8</td>
<td>2.408</td>
<td>1.019</td>
<td>64.6</td>
</tr>
<tr>
<td>4. Shell</td>
<td>278</td>
<td>1.115</td>
<td>0.504</td>
<td>64.8</td>
<td>2.342</td>
<td>1.006</td>
<td>64.4</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>478</td>
<td>1.790</td>
<td>0.879</td>
<td>68.9</td>
<td>3.672</td>
<td>1.717</td>
<td>68.0</td>
</tr>
<tr>
<td>6. Total</td>
<td>488</td>
<td>1.839</td>
<td>0.866</td>
<td>68.9</td>
<td>3.846</td>
<td>1.750</td>
<td>68.3</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>473</td>
<td>1.595</td>
<td>0.789</td>
<td>68.0</td>
<td>3.427</td>
<td>1.569</td>
<td>67.4</td>
</tr>
<tr>
<td>8. CPW PG 67-22</td>
<td>530</td>
<td>2.04</td>
<td>0.958</td>
<td>69.7</td>
<td>---</td>
<td>2.77</td>
<td>71.8</td>
</tr>
<tr>
<td>9. CPW PG 64-22</td>
<td>455</td>
<td>1.680</td>
<td>0.777</td>
<td>66.0</td>
<td>4.02</td>
<td>1.79</td>
<td>66.5</td>
</tr>
</tbody>
</table>

Note: P/F is the Pass/Fail temperature interpolated where G*/sinδ equals 1.0 kPa for original material and G*/sinδ equals 2.2 kPa for RTFO aged material.
### Table 3.3
**Intermediate Temperature Performance Grade Properties of Asphalt Cements**

<table>
<thead>
<tr>
<th>Asphalt Cement</th>
<th>RTFO/PAV Aged</th>
<th>G* sinδ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>19°C</td>
<td>22°C</td>
</tr>
<tr>
<td>1. Lion Oil</td>
<td>6.664</td>
<td>4.390</td>
</tr>
<tr>
<td>4. Shell</td>
<td>8.041</td>
<td>5.043</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>7.369</td>
<td>4.843</td>
</tr>
<tr>
<td>6. Total</td>
<td>7.125</td>
<td>4.670</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>6.802</td>
<td>4.754</td>
</tr>
<tr>
<td>8. CPW PG 67-22</td>
<td>5.380</td>
<td>3.750</td>
</tr>
<tr>
<td>9. CPW PG 64-22</td>
<td>7.080</td>
<td>4.770</td>
</tr>
</tbody>
</table>

P/F is the Pass/Fail temperature interpolated where G* sinδ equals 5.0 MPa and P-Tc is the low temperature grade if controlled by the intermediate stiffness.

### Table 3.4
**Low Temperature Performance Grade Properties of Asphalt Cements**

<table>
<thead>
<tr>
<th>Asphalt Cement</th>
<th>RTFO/PAV Aged</th>
<th>Stiffness S(60)</th>
<th>Slope m(60)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0°C</td>
<td>-6°C</td>
<td>-12°C</td>
</tr>
<tr>
<td>1. Lion Oil Company</td>
<td>206.0</td>
<td>453.0</td>
<td>-14.3</td>
</tr>
<tr>
<td>2. Exxon Mobil</td>
<td>195.0</td>
<td>414.0</td>
<td>-14.9</td>
</tr>
<tr>
<td>3. San Joaquin</td>
<td>155.0</td>
<td>449.0</td>
<td>-2.7</td>
</tr>
<tr>
<td>4. Shell</td>
<td>189.0</td>
<td>472.0</td>
<td>-8.4</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>360.0</td>
<td>569.0</td>
<td>-12.8</td>
</tr>
<tr>
<td>6. Total</td>
<td>215.0</td>
<td>454.0</td>
<td>-14.1</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>153.0</td>
<td>317.0</td>
<td>-17.4</td>
</tr>
<tr>
<td>8. CPW PG 67-22</td>
<td>97.1</td>
<td>198.0</td>
<td>403.7</td>
</tr>
<tr>
<td>9. CPW PG 64-22</td>
<td>252.0</td>
<td>478.0</td>
<td>-14.9</td>
</tr>
</tbody>
</table>

P/F is the Pass/Fail temperature interpolated where "s" equals 300 Mpa and where "m" equals 0.300. s-Tc and m-Tc are the corrected, grade controlling, critical temperatures, for "s" and "m" respectively, accounting for the M320 10°C testing temperature offset.
Table 3.5
Binder Grades for Asphalt Cements Tested

<table>
<thead>
<tr>
<th>Asphalt Cement</th>
<th>PG Grade</th>
<th>True Grade</th>
<th>UTI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lion Oil Company</td>
<td>64-22</td>
<td>65.0-24.3</td>
<td>89.3</td>
</tr>
<tr>
<td>2. Exxon Mobil</td>
<td>64-22</td>
<td>66.7-24.9</td>
<td>91.6</td>
</tr>
<tr>
<td>3. San Joaquin</td>
<td>64-4</td>
<td>64.6-9.6</td>
<td>74.2</td>
</tr>
<tr>
<td>4. Shell</td>
<td>64-16</td>
<td>64.4-16.2</td>
<td>80.6</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>64-22</td>
<td>68.0-22.8</td>
<td>90.8</td>
</tr>
<tr>
<td>6. Total</td>
<td>64-22</td>
<td>68.3-24.1</td>
<td>92.4</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>64-22</td>
<td>67.4-25.6</td>
<td>93.0</td>
</tr>
<tr>
<td>8. CPW PG 67-22</td>
<td>67-22</td>
<td>69.7-22.0</td>
<td>91.7</td>
</tr>
<tr>
<td>9. CPW PG 64-22</td>
<td>64-22</td>
<td>66.0-23.5</td>
<td>89.5</td>
</tr>
</tbody>
</table>

Asphalt cements 1 to 7 and 9 have upper grading limits of PG64, which was the target grade desired. From the results presented it can be seen that low temperature limits are stiffness ($s$) controlled on all binders with the exception of the Lion Oil Company and Orlen binders which are slope ($m$) controlled. An important observation is that the controlling parameter for the PADD 5 binders, San Joaquin and Shell Oil, both are low temperature stiffness “$s$” controlled by the intermediate temperature, PAV parameter, or PAV controlling temperature (PCT) grade, with the BBR “$s$” controlling temperature $sCT$ value not much lower than that calculated from the PAV parameter results (see table 3.3).

As stated, CPW PG 67-22 was selected due to its similar polymer compatibility characteristics to the original LO PG 64-22 and since it met specification requirements of the GADOT for the mixtures compared. Four asphalt binders were prepared and tested, using CPW PG 67-22 base asphalt, binder numbers 34 – 37. Table 3.7 presents the formulation of GTR wet binders, performance grading test results of all modified CPW
PG 67-22 modified binders will be discussed as part of the context of chapter 8. Table 3.7 presents the formulation of the GTR Wet modified binder.

Table 3.6

Formulation for GTR Wet Binder

<table>
<thead>
<tr>
<th>Material</th>
<th>Product</th>
<th>Weight %</th>
<th>Specific Gravity</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>CPW PG 67-22</td>
<td>89.55</td>
<td>1.02</td>
<td>88.88</td>
</tr>
<tr>
<td>Additive</td>
<td>TOR</td>
<td>0.45</td>
<td>0.98</td>
<td>0.47</td>
</tr>
<tr>
<td>GTR</td>
<td>GTR</td>
<td>10.0</td>
<td>0.95</td>
<td>10.66</td>
</tr>
</tbody>
</table>

3.2.3 Asphalt Cement Compositional Analysis

Each of the nine asphalt cements, was deasphaltened according to ASTM Method D-3279 “Standard Test Method for n-heptane Insolubles” to yield asphaltenes (A) the n-heptane insoluble portion and maltenes (Resins (R), Cyclics (C) and Saturates (S)) which is the n-heptane soluble portion (see Table 3.7).

The maltenes were further fractionated on an Iatroscan TH-10 Hydrocarbon Analyzer to yield the composition in saturates, cyclics and resins. The method has been described elsewhere (Raki et al. 2000, Masson et al. 2001). N-pentane was used to elute the saturates, and a 90/10 toluene/chloroform solution was used to elute the cyclics. The resins were not eluted and remained at the origin.
Table 3.7
Asphalt Cement Composition

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>A</th>
<th>R</th>
<th>C</th>
<th>S</th>
<th>A/(A+R)</th>
<th>Psh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lion Oil Company</td>
<td>10.4</td>
<td>9.3</td>
<td>78.1</td>
<td>2.2</td>
<td>0.53</td>
<td>8.07</td>
</tr>
<tr>
<td>2. ExxonMobil</td>
<td>13.2</td>
<td>14.1</td>
<td>68.1</td>
<td>4.6</td>
<td>0.48</td>
<td>7.80</td>
</tr>
<tr>
<td>3. San Joaquin</td>
<td>3.6</td>
<td>23.6</td>
<td>66.8</td>
<td>6.0</td>
<td>0.13</td>
<td>8.69</td>
</tr>
<tr>
<td>4. Shell</td>
<td>7.8</td>
<td>23.4</td>
<td>60.1</td>
<td>8.7</td>
<td>0.25</td>
<td>8.23</td>
</tr>
<tr>
<td>5. Total</td>
<td>12.3</td>
<td>13.1</td>
<td>71.5</td>
<td>3.1</td>
<td>0.48</td>
<td>7.90</td>
</tr>
<tr>
<td>6. Nynas</td>
<td>12.2</td>
<td>13.9</td>
<td>68.8</td>
<td>5.1</td>
<td>0.47</td>
<td>7.88</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>14.6</td>
<td>11.0</td>
<td>69.2</td>
<td>5.2</td>
<td>0.57</td>
<td>7.65</td>
</tr>
<tr>
<td>8. Conoco/Phillips</td>
<td>13.2</td>
<td>20.5</td>
<td>64.3</td>
<td>1.9</td>
<td>0.39</td>
<td>7.87</td>
</tr>
<tr>
<td>9. Conoco/Phillips</td>
<td>13.4</td>
<td>16.5</td>
<td>67.0</td>
<td>3.2</td>
<td>0.44</td>
<td>7.83</td>
</tr>
</tbody>
</table>

A relationship of asphaltenes to resins or asphaltenes to resins ratio is given by A/(A+R). A solubility parameter for the maltene fraction (Psh) is derived from the solubility parameters of solvents used in the thin layer chromatographic elution and the percentage of each component of the maltene fraction. Psh is a representation of the solvating power of the asphalt maltene fraction with higher numbers representing greater solvating power and lower numbers representing lesser solvating power (Meynard 1983).

Compositional analysis of asphalt binders may aid in identifying compatibility characteristics. Table 3.5 presents the performance grade for the base asphalt cements, true grade and UTI. Figure 3.1 shows the relationship of the solubility parameter (Psh) to the UTI. From Figure 3.1 and data presented in Tables 3.5 and 3.7, it is seen that binder’s lower values of Psh tend to exhibit wider UTI.
Polymers and GTR were typically used as received with no additional testing other than in modified asphalt formulations and in the TGA method development which will is discussed later in this dissertation.

Vector® 2411 (SBS), supplied by Dexco Polymers, was selected since it has been used in proprietary formulations for binders meeting AASHTO M320 PG 76-22 binder performance properties for projects in the Southeastern US. Vector® 2411 is a high molecular weight radial SBS triblock copolymer molecule composed of 30 percent poly(styrene) to 70 percent butadiene.
Vestenamer® 8012, trans-polyoctenamer (TOR) supplied by Evonik Industries, was selected due to claims of improved compatibility between asphalt binder and GTR. Vestenamer® 8012 TOR is used as a polymeric processing aid in a variety of rubber compounds for technical rubber goods and tires. It is used in difficult to process compounds incorporated into the polymer network and not extractable after curing. Vestenamer® 8012 polymer has also found applications in rubber recycling through addition of 4.5% of Vestenamer® 8012 added by weight of ground tire rubber. Claims are that the ground tire rubber is bonded to asphalt and the tackiness of the mixture is said to be completely lost.

Polyvulc USA, Inc. GTR from recycling of whole tires, was supplied in minus 850µm, 600 µm and 250 µm (minus 20, 30 and 60 mesh) sizes.

Twenty-Five rubber compounds were tested in the work of Chapter 5. Sixteen were compounded and supplied by Smithers Rapra North America of Akron Ohio. The remaining nine were random sampled 30/40 mesh from various GTR suppliers. Smithers Rapra (SR) prepared one compound with 100% natural rubber (NR), one compound with 100% styrene-butadiene rubber (SBR) and nine compounds varying the ratio of NR to SBR in 10% intervals, rubber compounds number 1 thru 11.

1. N100 – 100% NR;
2. S100 – 100% SBR;
3. N90/S10 – 90% NR / 10% SBR;
4. N80/S20 – 80% NR / 20% SBR;
5. N70/S30 – 70% NR / 30% SBR;
6. N60/S40 – 60% NR / 40% SBR;
7. N50/S50 – 50% NR / 50% SBR;
8. N40/S60 – 40% NR / 60% SBR;
9. N30/S70 – 30% NR / 70% SBR;
10. N20/S80 – 20% NR / 80% SBR;
11. N10/S90 – 10% NR / 90% SBR.

Five unknown compounds, compounds 12 thru 16, were prepared by SR identified only with letter designations A – E prior to TGA analysis. Post TGA analysis NR/SBR ratios were revealed.

12. Unknown A – reported by SR to be 100% NR;
13. Unknown B – reported by SR to be 64% NR / 36 % SBR;
14. Unknown C – reported by SR to be 43% NR / 57 % SBR;
15. Unknown D – reported by SR to be 37% NR / 63 % SBR;
16. Unknown E – reported by SR to be 100% SBR.

Nine additional 30/40 mesh GTR samples, GTR samples 17 thru 25, were obtained from various suppliers to be analyzed by the proposed TGA method for specification comparison purposes.

17. GTR 40;
18. Genan 30/40;
19. Global Type B;
20. Liberty Salt Lake;
21. Lehigh MD184 TR;
22. Lehigh MD400 TR;
23. Polyvulc 30/40 A;
3.4 Aggregates and Asphalt Mixtures

Granite aggregates, for mixture comparison testing and moisture sensitivity analysis specimens, were obtained from Rinker Material meeting the requirements as established by the Georgia DOT (GADOT, 2009).

For Group I binder comparative mixture work presented in Chapter 8, asphalt mixtures were prepared using a 12.5 mm (½ in.) nominal maximum aggregate size (NMAS) dense graded Superpave gyratory mix design, Open grade friction course (OGFC) Marshall 50 blow mix design (cellulose fibers), and SMA Superpave gyratory designed mixture as specified by GADOT (2009). The dense graded mixture contained a target binder content of 5.1% and was compacted to a nominal 6.0% air voids (6.0 + 1.0 via AASHTO T 166); the OGFC mix design contained a target binder content of 6.1% and was compacted to a nominal 20% air voids (20 + 2.0 via AASHTO T 269); while the SMA mix design contained a target binder content of 6.3% and was compacted to a nominal 6.0% air voids (6.0 +1.0 via AASHTO T 166). Dense graded and SMA mixtures can contain some (e.g., 10 to 20%) reclaimed asphalt pavement (RAP), however, in this study each mix type was produced with 100% virgin aggregate. The OGFC mixture contained 0.4% cellulose fibers as per mixture design requirements (GADOT, 2009).

All mixtures produced with GTR Wet and EAE PG 76-22 were produced with binder number 9, CP PG 64-22, at 171°C (340°F). Preheated aggregate was added to a
19 liter (5-gallon) bucket mixer and dry mixed. A well was made in the middle of the dry aggregate to which the binders were added and mixed until the aggregate was coated. The mixtures were AASHTO R 30, loose mixture, short or long term aged as appropriate for testing.

For each mix type, mixtures produced with GTR Dry were produced at 171°C (340°F). Preheated aggregate was added to a 19 liter (5-gallon) bucket mixer and dry mixed, then GTR/TOR was added dry. The resulting dry aggregate plus dry GTR mixture was then dry mixed again. A well was then made in the middle of the material to which the liquid PG 67-22 binder was added and mixed until coated. The mixture was AASHTO R 30, loose mixture, short or long term aged as appropriate for testing.

Limestone aggregates for mixture performance analysis specimens were tested from Mathy Construction meeting the requirements as established by the Wisconsin DOT (WIDOT, 2009).

Fine graded DGA mixture specimens with Group II binders, binders 39 thru 46 of section 3.2, in a 12.5mm (½-inch) NMAS Superpave gyratory mix design were prepared for mixture performance analysis. The dense graded mixture contained a target binder content of 5.3 % and was compacted to a nominal 4.0% air voids (4.0 ± 1.0 via AASHTO T166). Mixtures were produced at 171°C (340°F). Preheated aggregate was added to a 19 liter (5 gallon) bucket mixer and dry mixed. A well was made in the middle of the dry aggregate to which the binders were added and mixed until the aggregate was coated. Short term loose mix aging was performed as required by AASHTO R-30.
4.1 Overview of Experimental Program

This chapter covers the experimental program and rational of the overall program. After a brief discussion of how the specific objectives were chosen, the development of a general program to achieve each objective is explained. The bulk of work related to GTR asphalt modification reported in chapter 2 focused on evaluation of AR binders and mixtures containing AR. Not until the last 8 to 10 years has there been increased attention on RMA or terminal blended GTR, thus the focus of this dissertation is on RMA and its optimization. Though most often GTR is introduced directly into the asphalt binder, addition may be directly to the mixture at the same time as the aggregates, therefore, both are considered. Additionally, a processing aid is evaluated in combination with GTR modifier.

4.2 Focus of Specific Objectives and Their Focal Points

GTR modified binders provide a viable alternative for improving HMA and WMA performance by enhancing mix properties and reducing or delaying three general flexible pavement distress types: deformation (rutting and shoving), cracking (from
repeated loads and low temperatures) and general deterioration (raveling and stripping) (Terrel 1989).

The primary objective of this dissertation, to evaluate the importance of proper processing of GTR modified asphalt binders, addresses the secondary objectives presented in section 1.2. The rationale behind each of these objectives is discussed in the following sections and the experimental element designed to meet the stated objective is presented.

4.2.1 Characterization of GTR

As discussed in chapter 2, generally, throughout their lives, tires must fulfill a fundamental set of functions. To meet these requirements modern tires consist of the five primary components presented: tread, sidewall, steel belts, body plies, and the bead. Subsequently, tires are manufactured from a number of materials including natural and synthetic rubber, textiles and steel. Tire rubber is a complex and engineered, vulcanized compound, and, depending on their specific function and performance, different rubber formulations are based on different polymers and fillers. Additionally, low molecular weight ingredients are necessary for the various tire components. The rubber components are made using chemically stable and reactive/unstable materials. During tire manufacturing, reactive materials are generally consumed during the curing process, so that little, if any, of these materials are found in the finished product. There are actually hundreds of different tire formulations in existence and for the most part those formulations are proprietary to the individual tire companies as each manufacturer has developed their own compounds for particular usage.
Though the composition of a whole tire is complex, GTR from reclamation of old tires is somewhat different. With reactive and volatile materials being consumed in tire manufacturing and synthetic fibers and steel being removed in the GTR reclamation process the remaining GTR is generally comprised of natural and synthetic rubber; primarily NR and SBR cross-linked with sulfur and reinforced with carbon black. Other additives like aromatic hydrocarbons and antioxidants added to improve workability and prevent aging, respectively, are also present. Post-consumer, NR and SBR, polymers similar in chemical nature to virgin SB and SBS polymers currently used to modify asphalt, are the functional polymer compounds providing effective modification of asphalt binders making their nature and content in GTR of primary importance to effectiveness in GTR asphalt modification.

Currently there are two primary methods used to analyze tire rubber composition; 1) ASTM D297-13 Standard Methods for Rubber Products – Chemical Analysis; and 2) ASTM E1131-08 Standard Test Method for Compositional Analysis by Thermo-gravimetry. D297 is a two part collection of general test methods for quantitative and qualitative analysis of the composition of rubber products; part A methods are used in determination of some or all of the major constituents of a rubber product while part B covers indirect determination of specific polymers present in the rubber product. Analysis according to D297 is an extensive and relatively involved, process making it inconvenient for regular application to evaluate GTR. E1131 is a simpler empirical technique using thermo-gravimetry where mass loss over specific temperature ranges in specific atmospheres provide compositional analysis of that substance.
Practically, all of the elements related to GTR modification of asphalt binders and the use of GTR modified binder use in HMA presented in chapter 2 can benefit from a simple yet reliable method of compositional analysis of GTR recovered from scrap tires. Therefore, the focus of this objective is to develop a refined analytical method using techniques of E1131 to provide a suitable method for practical use in day-to-day evaluation of GTR used in asphalt modification. Better understanding of GTR composition should aid in proper use of GTR as a post-consumer polymer for modification of asphalt binders as well as its use in HMA mixtures. Compositional analysis of GTR from recovered scrap tires does not impact the reclaiming process, the way tires are made or their formulation; however, a useful method to identify content and availability of polymers from GTR reclamation may provide a means by which asphalt binder formulators can determine processing parameters and additional additives or processes necessary to produce optimized quality RMA formulations for use in HMA.

The merits of TGA as an affective instrumental analysis method to quantify and qualify the functional polymer, polymer available in GTR that is effective in modification of asphalt, and other chemical characteristics of post-consumer GTR is evaluated herein. This will be accomplished by analysis of prepared binary calibration standards of NR and SBR compounds used in pneumatic tire production, prepared unknown binary NR and SBR compounds and random samples of commercially available GTR from various suppliers.
4.2.2 Processing of GTR Modified Binders

In a paradigm shift to RMA binders from AR binders, processing and optimization of GTR modified asphalt binder formulations were accomplished in four evaluation phases to determine effects on binder properties:

- Phase I - GTR loading;
- Phase II - Processing temperature;
- Phase III - GTR particle size;
- Phase IV - Base asphalt source.

Testing of each of the GTR modified asphalt binders prepared in each of the four phases presented is in accordance with the methods and specifications listed in Table 4.1.

<table>
<thead>
<tr>
<th>Testing</th>
<th>Method/Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Performance Grade</td>
<td>AASHTO M 320</td>
</tr>
<tr>
<td>Original DSR with 2 mm Gap*</td>
<td>AASHTO T 315 @ 70, 76 and 82°C</td>
</tr>
<tr>
<td>Rotational Viscosity Profile</td>
<td>AASHTO T 316 @ 149, 163 and 177°C</td>
</tr>
<tr>
<td>Elastic Recovery</td>
<td>ASTM D 6048 (10 cm @ 25°C)</td>
</tr>
<tr>
<td>Separation</td>
<td>ASTM D 5976</td>
</tr>
<tr>
<td>UV Microscope Morphology</td>
<td>Paragon (PTSi) Internal Method</td>
</tr>
</tbody>
</table>

* In accordance with AASHTO M 320, the standard DSR test gap for paving asphalt binders is 1 mm.

AASHTO T 315 requires that particles within the asphalt be no larger than 0.25 mm, or one quarter of the total gap. GTR is not totally soluble in asphalt and the 850μm (20 mesh) GTR used in this study is more than four times the minimum particle specified by T 315, in addition, 850μm GTR contains some particles larger than 850μm. All of these factors can cause inaccurate DSR test results. Therefore, DSR testing on the GTR
modified binders was performed with both 1mm and 2mm test gaps to evaluate the effects of particle size on test results. This was addressed more specifically in the work of section 4.3.2 Testing and Specifications.

### 4.2.2.1 Phase I - Effect of GTR Loading

Lion Oil Company PG64-22 binder was modified with 5.0, 7.5 and 10.0% 850μm (20 mesh) GTR processed at 160°C (320°F). The processing temperature of 160°C (320°F) was selected as a starting point in consideration of information gleaned from the literature review related to temperature and degradation of GTR (Takallou 1992, Chahovits 1993). This temperature was also selected at the recommendation of the TOR additive supplier. As will be discussed in the next section, this temperature is considered to be too low to properly incorporate the GTR into a properly modified asphalt binder so other temperatures were considered in Phase II.

Addition of elemental sulfur to polymer modified asphalt binders containing polymers with unsaturated C-C double bonds is often used to improve the separation characteristics of the polymer modified asphalt binder. An additional modified binder was produced with the Lion Oil PG64-22 modified with 0.45% TOR and 10.0% 850μm (20 mesh) GTR processed at 160°C and post addition of 0.1% elemental sulfur in order to observe the effect of elemental sulfur on TOR/GTR modified asphalt binders.

### 4.2.2.2 Phase II - Effect of Processing Temperature

Processing temperature for proper modification is an important factor with any polymer modified binder whether modified with synthetic or post-consumer polymers.
While the temperature selected for Phase I was adequate to differentiate polymer loadings, all other parameters being equal, it is considered to be too low for proper binder modification. In a sense, the thermometer is a molecular speedometer for processing.

If one considers the relationship of two polymer properties, glass transition temperature (Tg) and melting temperature (Tm), adequate processing temperatures can be readily realized. In polymer chemistry, Tm is called the first-order transition temperature and Tg is referred to as the second-order transition temperature. Values of Tm are usually 33 to as much as 100% greater than Tg, and symmetrical polymers exhibit the greatest difference between Tg and Tm. To understand how this relates to the current discussion consider SBS, a common polymer used to modify asphalt binders. In SBS the Tg of the poly(butadiene) blocks is around -90°C (-130°F) and the Tg of the poly(styrene) is typically 100°C (212°F) so at any temperature between these two extremes SBS will act as a networked or physically cross-linked elastomer. Therefore, if SBS polymers are heated substantially above the Tg of the poly(styrene) blocks, 100°C (212°F), which happens to be the case at the typical minimum blending temperature of SBS modified asphalt binders of 180°C (356°F), the physical cross-links change from rigid glassy regions to flowable melt regions and the entire material flows and can be incorporated into the modified asphalt network establishing the inverse continuous phase discussed in chapter 2. Such is also the case of other polymer applications where polymers are heated above the Tg to allow them to cast, molded or extruded into desired form such as in the case of rubber compounds in the tire manufacturing process. On cooling this dispersed form resumes its elastomeric character which is the reason these materials are called thermoplastic elastomers (TPE). With SBS polymers it is not
uncommon to see processing temperature range from 180°C (356°F) toward 230°C (446°F) depending on specific polymer properties and SBS/asphalt formulation. More typical ranges are in the order of 180°C (356°F) to 200°C (392°F).

NR and SBR polymers used in manufacturing pneumatic tires have similar Tg and Tm properties to the SBS polymers discussed above (e.g. Tg SBR ~ -70°C). Additionally the molecular weights of the NR and SBR polymers used in tire manufacturing have similar molecular weights to SBS polymers used in production of SBS modified asphalt, in the range of 100,000 to 400,000 which is increased through the vulcanization process. Since Tg increases with increases in molecular weight, Tm also increases. This means an increase in the minimum temperature at which the rubber compound, or GTR, becomes flow able, same as with the SBS described above. The similarities between SBS and GTR dictate that minimum processing temperature for GTR asphalt modification should be at least equivalent to that of SBS asphalt modification, in the range of 180°C (356°F) to 200°C (392°F), perhaps higher depending on the molecular weight of the GTR. There is no reason the processing temperature for RMA should be lower than the typical tire molding temperature of 177°C (350°F).

To address determination of adequate processing temperatures for RMA, further evaluation was accomplished with Lion Oil Company PG 64-22 asphalt and 850μm (20 mesh) GTR as in Phase I except processing was at various temperatures. This evaluation aided in optimization of formulation and processing parameters as well as subsequent optimization of rubber particle size.

Temperature optimization consisted of four GTR modified binder blends processed at 160°C (320°F), 177°C 350°F (350°F), 193°C (380°F) and 210°C (410°F),
all prepared with low shear agitation. Each blend was tested as discussed in section 4.2.2, Table 4.1.

**4.2.2.3 Phase III - Effect of GTR Particle Size**

Studies have shown that, in addition to mixing temperature, GTR particle size, shape, and asphalt binder all effect the final GTR modified binder properties (Abdelrahman 1999, Loh et al. 2000, Baumgarnder et al. 2008, CalTrans 2005). As discussed in chapter 2, final properties are more due to swelling of the rubber particles than they are chemical behaviors. Final properties depend on proper dispersion of rubber particles and solubility in the asphalt binder (Chehovits 1993). Reaction time and final properties depend on temperature, GTR particle size, dispersion efficiency and shearing forces during blending. Improved dispersion and finer GTR particles may be used to reduce reaction time and temperature. The time to fully react has been stated to be a direct function of the GTRs relative surface area (Lynch 1986, Rouse 1994a, Rouse 1994b, Lehigh 2015).

The optimal temperature determined from Phase II using 20 mesh ground tire rubber was extended to formulations with 30 and 60 mesh ground tire rubber in order to better understand effects of rubber particle size. This resulted in a total of two GTR modified asphalt blends. Each blend shall be tested as discussed in section 4.2.2, Table 4.1, as with the previous phases.
4.2.2.4 Phase IV - Effect of Asphalt Source

From chapter 2 it is understood that several factors may affect the reaction between polymer and asphalt such as blending time (González et al. 2012), blending temperature (Navarro et al. 2007), relative surface area (particle size, texture and dispersions) (West et al. 1998, Putman et al. 2006, Shen et al. 2009). Compatibility between polymer and asphalt binder is also important for the reaction to fully occur which improves the binder characteristics (Chehovits 1992, Buncher 1995, Brule 1996, Daly et al. 1997, Ariez et al. 2002, Artamendi et al. 2006). Compatibility is governed by polymer and asphalt chemical composition. Compatibility is normally demonstrated when the polymer is blended with the asphalt binder and properties improve to a desired level and stabilized within a reasonable period of time at a reasonable temperature. Synthetic polymers are produced with consistent properties which can generally be selected and adjusted to design polymers with asphalt compatible characteristics. Additionally, most GTR produced from scrap tires, as of the date of this dissertation, consist of a relatively homogeneous blend of different rubber polymers making compatibility more of a matter of asphalt composition than GTR composition. Asphalt chemical composition can vary greatly depending on crude source.

Upon completion of the first three phases, optimum parameters identified with Lion Oil PG64-22 were extended to the additional asphalt binders presented in Table 3.1. Formulations with 10% of the optimum particle size rubber as determined from the Phase III study were evaluated with each of these asphalts using the optimum processing temperatures as determined from the phase II study. This resulted in a total of six GTR
modified asphalt binders, and each binder was tested as discussed in section 4.2.2, Table 4.1.

4.2.3 Testing and Specifications

As discussed in chapter 2, specifications for GTR modified asphalt binders in most applications have been recipe or method type where very specific process and amounts of material are called for to produce a specific product. In cases where contractors have experience with these specifications good performance can be achieved (Heitzman 1992, Epps 1994). However, this makes transfer of these processes and specifications very difficult from one location to another and increases the potential for failures (CalTrans 2005).

Rudimentary test procedures have been tried to provide some type of quality control for the various processes. The primary device is the hand held rotational viscometer (Epps 1994). This can provide some indication of viscosity increase from the addition and blending of rubber into the binder but has high variability. Binder testing has been performed using the Superpave binder tests on RMA binder but this has been limited to GTR sizes that can be handled in the 1 mm or 2 mm gap using parallel plate geometries (Abdelrahman 1999, Loh et al. 2000, Baumgarnder et al. 2008), which are typically 30 mesh material or smaller. These studies did show the increase in modulus of the binder with addition of the GTR and that the size, percentage of rubber and base asphalt all had an effect on the binder properties. However, in general use GTR comes in many different sizes and the most used material is typically larger than the 30 mesh. This requires testing of the binder with larger particle sizes using geometries with larger gaps.
Without a well-defined binder specification, adoption of the use of RMA binder by US highway agencies will be almost impossible to achieve. Test procedures that can evaluate the performance characteristics of RMA binder are crucially needed.

Rheological testing of binders is now a standard practice to evaluate performance characteristics of neat and modified binders. Superpave specifications do have limitations that restrict materials that can be tested. Existing specifications use the dynamic shear rheometer (DSR) and plate/plate geometry with a 1 mm gap for testing of binders at high and intermediate temperatures (Petersen 1994). This geometry limits the materials that can be tested between the plates. Particulate matter larger than 250 μm cannot be tested due to the possible interaction of particulate matter on torque and strain response of the binder (Petersen 1994). Typical AR binder has rubber particles much larger than 250 μm. Rubber particles may range in size from 0.5 mm (500 μm) up to over 1 mm (1000 μm) in size. A 1 mm particle tested in a DSR with a 1 mm gap parallel plate geometry would be touching both top and bottom plates at the same time so test results would represent the rubber particle not a rubber modified binder.

Performing PG testing on GTR modified binders with larger particles will require using new geometries that provide larger gaps that can accommodate larger particles. One approach that has been used in the food industries has been testing with concentric cylinder geometries. DSRs currently used for asphalt testing can be adapted to use a Searle system where the center cylinder or bob rotates and the outside cylinder or cup is stationary (Schramm 1994, Steffe 1996). This type of system can perform all the same types of testing that are currently used for asphalt binder grading. The advantage is that the cup and bob geometry can easily handle larger gaps up to 4 to 7 mm, and therefore...
accommodate the larger GTR particles. The Searle, Cup and Bob, system was used to evaluate GTR modified binders in comparison to standard parallel plate geometry testing according to Superpave guidelines.

### 4.2.4 Mixture Evaluations

While dry addition of GTR to asphalt mixture is not a new concept and earlier versions of dry process GTR had limited results, chapter 2 presented a new method of dry mixture addition used today referred to as BAM or belt add modifier. BAM contain additional additives such as polymers, TOR, or waxes to provide improved mixing and compaction characteristics. These additives are believed to do more in improving mixing and compaction than actually function as a property modifier of the base asphalt. In a sense BAM additives act more like mixture added WMA additives than asphalt binder modifiers. As with the dry addition methods of yesteryear, a primary concern with BAM is whether there is sufficient time in the HMA mixing process to allow for expected binder modification (Lougheed et al. 1996, Moreno et al. 2011).

In chapter 2 it was reported that (Moreno et al. 2011) suggested that the optimum GTR content and digestion time for dry mixture addition was 1% and 90 minutes respectively. This would equate to a GTR loading of from 16 to 20% based on the binder contents used in the Moreno work. As of the date of this dissertation, common GTR loadings allowed in available BAM systems are much less, generally 10% dry added GTR based on asphalt binder content. The more common BAM system uses TOR at an addition rate of 4.5% based on GTR loading, or 10% GTR and 0.45% TOR based on asphalt binder content. Considering a fixed binder content of 5.0%, this equates to a
dry mixture addition rate of 0.5225 BAM or 0.5% GTR and 0.0225% TOR or 10.45 pounds of BAM per ton of HMA. Considering the lesser amount of GTR compared to (Moreno et al. 2011), digestion time for this level of BAM may possibly be reduced.

The fourth and final secondary objective was related to asphalt binders used in three primary applications: dense graded asphalt (DGA), stone matrix asphalt (SMA) and open graded friction courses (OGFC). Laboratory tests were conducted to determine whether DGA, OGFC, and SMA mixtures can be produced with BAM in the form of GTR/TOR added both to the mix dry and wet blended into asphalt to meet standard PG76-22 specification requirements. Based on information presented in chapter 2 it is understood that some binders may require greater than 10% GTR by weight of asphalt binder to achieve a PG grading of PG76-22. However, 10% by weight of asphalt is selected for this work to represent loadings currently specified by some agencies for commercially available BAM processes implied to provide performance equivalent to PG76-22 modified binders. It is understood that a higher loading of GTR would serve to improve PG grade performance. To determine the effect of the commonly specified 10% BAM addition versus wet blending of GTR at the 10% loading. Comparisons were made to commercially available PG 76-22 formulated to meet the PG 76-22 specification requirements. GTR/TOR wet and BAM were compared with DGA, OGFC and SMA mixtures using PG76-22 modified with SBS.
In addition to standard binder testing on prepared and extracted binders, mixture testing was performed to address the primary mixture failure modes. Mixture evaluation testing consisted of:

- Cantabro mixture durability;
- Asphalt Pavement Analyzer (APA) rut testing;
- Hamburg Wheel Tracking Device (HWTD) rut testing;
- DSR repeated creep (RC) testing;
- Texas Overlay Test (TXOT) fatigue testing;
- Bending Beam Rheometer (BBR) mixture beam testing;
- Asphalt Mixture Performance Tester (AMPT) dynamic modulus testing.
CHAPTER 5

THERMO-GRAVIMETRIC TEST RESULTS

5.1 Overview of Thermo-Gravimetric Results

Key findings of this chapter have been published in *Road Materials and Pavement Design* (Baumgardner et al. 2014) and presented at the 89th annual meeting of the Association of Asphalt Paving Technologists (AAPT).

Adequate analysis and understanding of the functional polymer content, polymer available in GTR to improve asphalt binder properties, and other chemical characteristics of GTR remains lacking. This chapter presents an instrumental thermo-gravimetric analysis (TGA) method to analyze GTR for better understanding and quantification of the functional polymer content, as well as general chemical characteristics, of GTR used to modify asphalt binders.

Currently there are two primary methods used to analyze tire rubber composition, ASTM D297-13 Standard Methods for Rubber Products – Chemical Analysis and ASTM E1131-08 Standard Test Method for Compositional Analysis by Thermo-gravimetry. D297 is a two part collection of general test methods for quantitative and qualitative analysis of the composition of rubber products; part A methods are used in determination of some or all of the major constituents of a rubber product while part B covers indirect determination of specific polymers present in the rubber product. Analysis according to
D297 is an extensive, and relatively involved, process. E1131 is a simpler empirical technique using TGA where mass loss over specific temperature ranges in specific atmospheres provide compositional analysis of that substance.

In TGA, the change in mass of a material is measured as a function of temperature or time. TGA facilitates acquisition of information on properties of a material and its composition. When a sample is heated it often loses mass. Loss of mass may be caused by vaporization or chemical reactions which evolve gaseous products from the sample. In material decomposition as a result of chemical reaction, the mass of the sample often changes in a stepwise manner. The temperature at which steps occur provides information on the stability of the material in the atmosphere used. For example if a reactive gas atmosphere is used, reaction of the material with the gas can result in mass change. Typically this mass change is exhibited in the form of mass loss, however, in cases such as oxidation there may be a gain in mass. Composition of a material can be determined by analyzing the temperatures and the heights of the individual weight loss steps.

TGA can be used as a way to measure the thermal stability of a polymer and the thermal degradation of polymer blends due to the simplicity of the weight loss method (Schawe 2002). The potential of TGA for quantitative analysis of vulcanizates based on binary elastomer blends of NR and SBR has been previously reported (Sircar et al. 1975, Brazier et al. 1975, Lee et al. 2007). Figure 5.1 is an example of a TGA curve, also known as a thermogram (TG), from analysis of a rubber compound.

Volatile compounds such as water, residual solvents, or oils are evolved at relatively low temperatures, step height of Figure 5.1, Region 1. Analysis of pyrolysis
reactions in an inert atmosphere, step height of Figure 5.1, Region 2 allows determination of the content and type of material. Carbon black is determined from the step height of the combustion step, Figure 5.1, Region 3 and residual ash or filler is determined from the residue, Figure 5.1, Region 4.

![Figure 5.1](image)

**Schematic of TGA Curve**

Note: Region 1 - loss of mass through vaporization, Region 2 - pyrolysis, Region 3 - combustion of carbon on switching from an inert to oxidative gas, Region 4 – residue.

### 5.2 Calibration Sample Preparation

Eleven rubber compounds, listed as rubber compounds numbers 1 to 11 in Section 3.3 of this dissertation, were prepared as calibration samples for TGA method development. One compound with 100% natural rubber (NR), one compound with 100% styrene-butadiene rubber (SBR) and nine binary rubber blends of NR and SBR
compounds were prepared by Smithers Rapra North America of Akron Ohio. A generic CV60 grade natural rubber was used. The SBR (COPO® 1500) was produced by Lion Copolymer., Ltd., and is a random copolymer with a styrene content of 23.5 weight percent. These NR and SBR grades were chosen because of their wide uses in rubber industries. Carbon black is used in various formulations with different rubber types to customize performance properties; N339 was used in these formulations as it is a common grade used in premium passenger tire tread compounds. Other compounding materials such as a vulcanizing agent (sulfur) and accelerator are fairly common and were selected from commercially available grades.

Five additional compounds, rubber compounds 12 to 16 of Section 3.3, with unknown NR/SBR ratios and content, were incorporated as unknown compounds for subsequent analysis to test the potential of the method presented. These compounds were also prepared by Smithers Rapra. Identical raw materials as described above were used in preparation of these compounds.

NR/SBR blends were prepared with the blend ratios in the range from 0 to 100% NR. Additives were compounded in the same proportions to prepare all the blends (stearic acid: 2.0 phr, ZnO: 4.0 phr, carbon black: 65 phr, accelerator: 1.0 phr, sulfur: 2.0 phr). Nearly all compounders use the unit of measure of "parts per hundred" (phr) for their formulations. Phr is a unit of weight for the relationship between the rubber (NR, SBR) component and the other components in the compounds. For example, if 100 parts of rubber is always utilized for all compound formulas then it is much simpler to change the other components in the compound to create changes and different formulas. The reason this is so important is that the cure system reacts only with the rubber system.
Thus, if all the other components are changed, the relationship between the rubber component and the cure component remain constant with only a few exceptions. A close weight percent approximation of the rubber compounds prepared as above would be 64 % volatile substances and rubber hydrocarbon and 36 % carbon black and non-volatile residue. Specifically at 100 phr rubber and 65 phr carbon black the weight percent approximation would be approximately 60 % rubber hydrocarbon and 40 % carbon black.

For this study, the rubber compounds were mixed in a Farrell internal mixer of a two-wing, tangential approach. A rotor speed of 55 rpm and a heat exchanger temperature of 65°C were used. The fill factor was established at 0.75. The master pass mixing cycle in the Farrell mixer mixed the polymers for 0.5 min, added carbon black, zinc oxide, and stearic acid, mixed until the batch reached 160°C (320°F), dumped the compound, sheeted it out with a 254 mm (10 inch) mill and conditioned it for > 16 hours. A rotor speed of 30 rpm and a heat exchanger temperature of 43°C (109°F) were used for the finish pass. The fill factor of the finish was established at 0.75. The finish mixing cycle in the Farrell mixer mixed the polymers for 0.5 minutes, added the curatives, mixed until the batch reached temperature, dumped the compound, sheeted it out, and let it condition for > 16 hours. The material was blended to fixed percentages conducted on a 152 mm (6 inch) mill, which was followed by sheeting. The NR and SBR are denoted by N and S series, respectively. The blend composition is denoted as Nx/Sy (NR x %, SBR y %), where x and y indicate the weight percentage of each rubber.
5.3 TGA Procedure

Thermal degradation studies were performed on a TA Instruments 2950 thermogravimetric analyzer using 10.0 ± 0.5 mg samples to eliminate any sample size effects. The initial purge gas, Nitrogen (N2), flow rate to the TGA was set at 40 mL/min from 40 °C (104°F) to 550°C (1022°F). Sample temperature was allowed to equilibrate at 40°C (104°F) where isothermal conditions were maintained for 3 min. Sample temperature was then ramped from 40°C (104°F) to 300°C (572°F) at a heating rate of 20 °C/min (68°F/min) and held in isothermal conditions for an additional 20 min. Further heating of the sample was performed ramping from 300°C (572°F) to 550°C (1022°F) at a heating rate of 20 °C/min (68°F/min) and held in isothermal conditions for an additional 5 minutes. At this point the purge gas was changed to air with the flow rate to the TGA set at 40 mL/min and the sample temperature was increased to 750°C (1382°F) at a heating rate of 20 °C/min (68°F/min) and held in isothermal conditions for an additional 5 min. Finally the purge atmosphere was changed to N2 and heating continued until a constant weight was achieved at 750°C (1382°F). The following summary presented in the following is a method log of the TGA protocol:

1: Select Gas 1: N2
2: Equilibrate at 40.00°C
3: Isothermal for 3.00 min
4: Data storage: On
5: Ramp 20.00°C/min to 300.00°C
6: Isothermal for 20.00 min
7: Ramp 20.00°C/min to 550.00°C
8: Isothermal for 20.00 min
Output from the thermal degradation analysis method was presented graphically plotting change in mass versus change in time to produce the stepwise TGA thermal degradation curve, TG, previously discussed. A curve representing the derivative of the stepwise TG was also plotted (DTG). A summary of the output is presented in the following analysis method log:

X axis = Time

Y axis = Weight loss

Second Y axis = derivative of weight loss with respect to time (DTG).

Region one:
Analyze weight change

Manual limits 0 minutes to 25 minutes

Label: Acetone Extract

Region two:
Analyze Weight change

Manual limits 25 minutes to 50 minutes

Label: RHC

Region three:
Typical results from this method of the TG curve and the DTG curve outputs are presented in Figure 5.2. Weight loss steps on the TGA output appear as downward slopes of the TG curve and peaks in the DTG curve. The slope of the TG curve corresponds to the rate of change of sample mass. In region 1, volatile compounds such as water, residual solvents and oils are evolved from 0 to 25 minutes at relatively low temperatures from 40 to 250°C (104 to 482°F). In region 2, pyrolytic decomposition occurs in an inert atmosphere (nitrogen) from 25 to 50 minutes at 250 to 550°C (482 to 1022°F) (Juma et al. 2006), allowing for analysis of the content (step height) and material type of the rubber hydrocarbon component. The carbon black content is determined from the step height of the combustion region 3, which occurs, after switching to the oxidative (air) atmosphere, from 50 to 70 minutes at 550 to 750°C (1022 - 1382°F). Region 4 is residual ash resulting as residue remaining from the entire TGA process.
Of noteworthy importance from Figure 5.2 is that regions 1 and 2 make up the original approximation of 64 % volatile and rubber hydrocarbon components of the original compound and regions 3 and 4 make up the original 36 % carbon black and non-volatile components of the original compound. Therefore the functional polymer component as derived from the TGA analysis is represented by the 48.86 % of region 2.
5.4 Analysis of Calibration Samples

Materials of binary, NR/SBR, compounds were decomposed in nitrogen between 250 and 550°C (482 to 1022°F), the same as in (Juma et al. 2006). As all polymers are pyrolyzed, thermal decomposition converts the weight % at the initial temperature into 100% and the weight % at 550°C (1022°F) into 0% to exclude the weight effect of carbon black and filler remaining in the sample (Shield et al. 2001). The TG and DTG curves of rubber compound number 1, N100, and rubber compound number 2, S100, are presented in Figure 5.3. In Figure 5.3, DTG curves in nitrogen are characterized by well-defined peaks for each polymer at 100% loading levels.

![Figure 5.3](image)

Figure 5.3

Weight Loss TG Curves/DTG Curves, N100 and S100 Rubber Compounds

Figure 5.4 shows the TGs (a) and DTG curves (b) for the NR/SBR compounds, note that the SBR content in the TGs increase from left to right and the shape of the DTG curve changes correspondingly with respect to the ratio of NR to SBR. A summarization
of TG and DTG, NR and SBR, peak data for the eleven calibration compounds is presented in Table 5.1. Figure 5.4 presents a calibration curve of DTG peak height (% weight loss/min) versus NR content constructed from the NR data presented in Table 5.1.

Data below 40% NR are not plotted in Figure 5.4 as it should be noted that with lower concentrations of either NR or SBR as a percent of total polymer, less than about 30%, it may be necessary to rely on calibration curves representing the stronger peak. For example, a compound with NR content less than about 30% of total polymer may require comparison to a calibration curve prepared from SBR peak properties for more accurate results. Therefore, a similar calibration curve of DTG peak height (% weight loss/min) versus SBR content with similar statistical accuracy to Figure 5.5 was also prepared from the SBR data in Table 5.1 but is not presented in consideration of brevity.

Similar correlations can be made in comparison to area under the DTG curves; however, peak height comparison is more straightforward.
Figure 5.4

TG Weight Loss Curves (a) and DTG Curves (b) Comprised between N100 (first left) Increasing SBR by 10% Increments to S100 (last right)
Table 5.1

Calibration Compound TG and DTG Peak Data from TGA

<table>
<thead>
<tr>
<th>Sample N%/S% (1.0 smoothing)</th>
<th>Natural Rubber</th>
<th>Styrene Butadiene Rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>Temp °C</td>
<td>TG %</td>
</tr>
<tr>
<td>1. N100</td>
<td>40.7</td>
<td>388.7</td>
</tr>
<tr>
<td>3. N90/S10</td>
<td>40.8</td>
<td>390.4</td>
</tr>
<tr>
<td>4. N80/S20</td>
<td>40.8</td>
<td>390.1</td>
</tr>
<tr>
<td>5. N70/S30</td>
<td>40.7</td>
<td>388.9</td>
</tr>
<tr>
<td>6. N60/S40</td>
<td>40.7</td>
<td>388.9</td>
</tr>
<tr>
<td>7. N50/S50</td>
<td>40.8</td>
<td>390.4</td>
</tr>
<tr>
<td>8. N40/S60</td>
<td>41.0</td>
<td>393.8</td>
</tr>
<tr>
<td>9. N30/S70</td>
<td>41.0</td>
<td>394.8</td>
</tr>
<tr>
<td>10. N20/S80</td>
<td>41.0</td>
<td>395.6</td>
</tr>
<tr>
<td>11. N10/S90</td>
<td>41.2</td>
<td>397.2</td>
</tr>
<tr>
<td>2. S100</td>
<td>44.3</td>
<td>460.4</td>
</tr>
</tbody>
</table>

Note: Numbers 1 to 11 denote Section 3.3 rubber compound IDs.

Figure 5.5

NR Calibration Curve DTG Data for Known NR/SBR Compounds
5.5 Analysis of Prepared Unknowns

Figure 5.6 presents composite TG and DTG output from analysis of five laboratory prepared vulcanized NR/SBR unknown compounds of varying NR to SBR ratios, rubber compounds 12 to 16. Analysis of the DTG curves for each compound as compared to the calibration curve produced from data in Table 5.1 allows estimation of the NR percent in comparison to SBR percent. Results of unknown compound TG and DTG peak analysis are presented in Table 5.2. The overall height of region 2 for each of the TG curves indicates the total polymer content, NR/SBR. TG analysis results for acetone extract, total polymer, NR content, SBR content, carbon black, and ash from comparison to the NR calibration curve are presented in Table 5.3. From (Lee et al. 3007) as noted in section 5.4, with lower concentrations of either NR or SBR as a percent of total polymer, less than about 30%, it may be necessary to rely on calibration curves representing the stronger peak. For example, a compound with NR content less than about 30% of total polymer, such as compounds D and E, and SBR contents less than 30% of total polymer, such as A and B, may require comparison to a calibration curve prepared from SBR peak properties for more accurate results.
Figure 5.6
TG and DTG Output for Five Prepared Unknown NR/SBR Compounds

Table 5.2
Results from TGA Analysis of Prepared Unknown NR/SBR Compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>Temp °C</th>
<th>TG %</th>
<th>DTG %/min</th>
<th>Time (min)</th>
<th>Temp °C</th>
<th>TG %</th>
<th>DTG %/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>12. A</td>
<td>37.5</td>
<td>382.1</td>
<td>58.9</td>
<td>11.3</td>
<td>39.7</td>
<td>426.2</td>
<td>46.3</td>
<td>6.7</td>
</tr>
<tr>
<td>13. B</td>
<td>37.6</td>
<td>383.2</td>
<td>63.9</td>
<td>9.9</td>
<td>40.6</td>
<td>443.2</td>
<td>47.8</td>
<td>9.0</td>
</tr>
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<td>14. C</td>
<td>37.7</td>
<td>385.5</td>
<td>69.9</td>
<td>6.6</td>
<td>40.8</td>
<td>447.8</td>
<td>50.5</td>
<td>11.3</td>
</tr>
<tr>
<td>15. D</td>
<td>72.4</td>
<td>395.6</td>
<td>38.2</td>
<td>5.6</td>
<td>41.2</td>
<td>455.8</td>
<td>51.8</td>
<td>15.4</td>
</tr>
<tr>
<td>16. E</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Numbers 12 to 16 denote Section 3.3 rubber compound IDs.
Table 5.3

Composition of Prepared Unknown Compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetone Extract %</th>
<th>Total Polymer %</th>
<th>Natural Rubber %</th>
<th>SBR %</th>
<th>NR/SBR Ratio</th>
<th>Carbon Black %</th>
<th>Ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>12. A</td>
<td>20</td>
<td>45</td>
<td>45</td>
<td>0</td>
<td>100/0</td>
<td>33</td>
<td>2</td>
</tr>
<tr>
<td>13. B</td>
<td>17</td>
<td>48</td>
<td>31</td>
<td>17</td>
<td>64/36</td>
<td>33</td>
<td>2</td>
</tr>
<tr>
<td>14. C</td>
<td>18</td>
<td>47</td>
<td>20</td>
<td>27</td>
<td>43/57</td>
<td>33</td>
<td>2</td>
</tr>
<tr>
<td>15. D</td>
<td>17</td>
<td>48</td>
<td>18</td>
<td>30</td>
<td>37/63</td>
<td>33</td>
<td>2</td>
</tr>
<tr>
<td>16. E</td>
<td>17</td>
<td>48</td>
<td>0</td>
<td>48</td>
<td>0/100</td>
<td>33</td>
<td>2</td>
</tr>
</tbody>
</table>

5.6 Practical Applications

5.6.1 Analysis of GTR Samples - Specification Compliance

In accordance with (FLDOT 2013) chemical requirements for composition of GTR shall be determined in accordance with ASTM D297 and shall meet the following requirements:

Acetone Extract .................................................. Maximum 25%

Rubber Hydrocarbon Content ................................. 40 to 55%

Natural Rubber ..................................................... 16 to 45%

Carbon Black Content ........................................... 20 to 40%

Ash Content ....................................................... Maximum 8%

ASTM D297 is an adequate method of analysis of GTR composition, however, as previously stated it is somewhat more involved than the proposed instrumental method and more than likely would not be performed on a regular basis. The proposed method is therefore considered more “user friendly” and can be incorporated into an effective materials quality control program.
Figure 5.7 presents TGA output from analysis of vulcanized NR/SBR from a random GTR sample from scrap tires identified as GTR40. The overall height of region 2 of the TG curve indicates that the total polymer content, NR/SBR of the GTR 40 sample is 52.46%.

![TGA Output for GTR40, TG and DTG Curve](image)

The DTG curves in nitrogen, Figure 5.8, are characterized by similar well-defined peaks for each polymer, which have been previously illustrated. The degradation peak for NR is approximately 388°C (730°F) in comparison to approximately 439°C (820°F) for SBR. The peak temperature for NR is separated from that of SBR by approximately 51°C (90°F). It is, therefore, possible to characterize NR and SBR in the NR/SBR compounds as previously reported in the literature (Schawe 2002, Lee et al. 2007).
Figure 5.8

DTG Curves from TGA of GTR 40 Sample

DTG peak values for NR and SBR are 8.280 %/min and 8.472 %/min. Using the NR DTG data from the GTR40 TGA analysis, presented in Table 5.3, in relationship to the calibration curve, it is possible to determine from Figure 5.9 that the 52.46 % total NR/SBR polymer content of the GTR40 sample is comprised of approximately 54 % NR (53.93 % calculated from a linear fit) and approximately 46 % SBR (46.07 % calculated by difference).
Table 5.4 presents analysis data, analyzed as above, from the GTR40, GTR sample 17 from Section 3.3, and eight samples of GTR, GTR samples 18 to 25 of Section 3.3, randomly sampled from various industry suppliers.

Table 5.4

Results from TGA Analysis of Random GTR Samples

<table>
<thead>
<tr>
<th>Sample N%/S%</th>
<th>Time min</th>
<th>Temp °C</th>
<th>TG %</th>
<th>DTG %/min</th>
<th>Time min</th>
<th>Temp °C</th>
<th>TG %</th>
<th>DTG %/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>17. GTR40</td>
<td>40.7</td>
<td>387.7</td>
<td>72.9</td>
<td>8.28</td>
<td>43.2</td>
<td>438.6</td>
<td>53.8</td>
<td>8.5</td>
</tr>
<tr>
<td>18. Genan 30/40</td>
<td>37.5</td>
<td>382.3</td>
<td>72.0</td>
<td>7.1</td>
<td>38.9</td>
<td>429.8</td>
<td>55.0</td>
<td>7.7</td>
</tr>
<tr>
<td>19. Global Type B</td>
<td>37.5</td>
<td>382.4</td>
<td>65.9</td>
<td>8.3</td>
<td>39.2</td>
<td>416.3</td>
<td>52.4</td>
<td>8.0</td>
</tr>
<tr>
<td>20. Liberty Salt Lake</td>
<td>37.5</td>
<td>381.4</td>
<td>69.2</td>
<td>8.4</td>
<td>39.6</td>
<td>423.2</td>
<td>53.2</td>
<td>7.6</td>
</tr>
<tr>
<td>21. Lehigh MD 184</td>
<td>37.6</td>
<td>384.5</td>
<td>69.1</td>
<td>7.3</td>
<td>39.8</td>
<td>428.6</td>
<td>53.0</td>
<td>7.7</td>
</tr>
<tr>
<td>22. Lehigh MD 400</td>
<td>37.4</td>
<td>379.0</td>
<td>72.3</td>
<td>7.5</td>
<td>47.7</td>
<td>435.6</td>
<td>51.7</td>
<td>7.8</td>
</tr>
<tr>
<td>23. Polyvulc 30/40 A</td>
<td>37.4</td>
<td>379.0</td>
<td>68.2</td>
<td>7.9</td>
<td>40.6</td>
<td>443.5</td>
<td>44.0</td>
<td>8.3</td>
</tr>
<tr>
<td>24. Polyvulc 30/40 B</td>
<td>37.5</td>
<td>381.3</td>
<td>71.4</td>
<td>7.5</td>
<td>40.1</td>
<td>434.5</td>
<td>52.1</td>
<td>7.8</td>
</tr>
<tr>
<td>25. Florida Type B</td>
<td>37.4</td>
<td>380.1</td>
<td>71.1</td>
<td>7.9</td>
<td>39.6</td>
<td>423.0</td>
<td>55.4</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Note: Numbers 14 to 25 denote Section 3.3 GTR sample IDs.
Table 5.5 presents compositional analysis from the GTR40 and the eight random GTR samples in comparison to the specification in accordance with (FLDOT 2013). For the most part, all samples tested met specification requirements with the exception of the ash content of sample eight. GTR sample 23 and 24 are actually duplicate sample runs at different times to check reproducibility.

Table 5.5
Composition of Random GTR Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetone Extract %</th>
<th>Total Polymer %</th>
<th>Natural Rubber %</th>
<th>SBR %</th>
<th>Carbon Black %</th>
<th>Ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>17. GTR 40</td>
<td>11</td>
<td>53</td>
<td>28</td>
<td>24</td>
<td>29</td>
<td>7</td>
</tr>
<tr>
<td>18. Genan 30/40</td>
<td>14</td>
<td>46</td>
<td>21</td>
<td>24</td>
<td>31</td>
<td>9</td>
</tr>
<tr>
<td>19. Global Type B</td>
<td>17</td>
<td>45</td>
<td>24</td>
<td>21</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>20. Liberty Salt Lake</td>
<td>15</td>
<td>47</td>
<td>26</td>
<td>21</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>21. Lehigh MD 184</td>
<td>16</td>
<td>45</td>
<td>22</td>
<td>24</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>22. Lehigh MD 400</td>
<td>15</td>
<td>48</td>
<td>23</td>
<td>24</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>23. Polyvulc 30/40 A</td>
<td>16</td>
<td>51</td>
<td>26</td>
<td>25</td>
<td>29</td>
<td>4</td>
</tr>
<tr>
<td>24. Polyvulc 30/40 B</td>
<td>15</td>
<td>48</td>
<td>23</td>
<td>24</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>25. Florida Type B</td>
<td>14</td>
<td>45</td>
<td>23</td>
<td>22</td>
<td>28</td>
<td>13</td>
</tr>
<tr>
<td>Spec</td>
<td>&lt; 25%</td>
<td>40-55%</td>
<td>16-45%</td>
<td>NA</td>
<td>20-40%</td>
<td>&lt; 8%</td>
</tr>
</tbody>
</table>

5.6.2 Binder Formulation

The simplest application of this method would be in verification of compliance of raw materials to established specifications such as FDOT (FDOT 2013). However, TGA measured data has broader applicability in formulation of modified binders as well as in mix design.

Data as presented in Table 5.5 could prove to be quite useful in modified asphalt binder formulation. To date the bulk of work related to studying effects of GTR in modified asphalt binders has focused on GTR as a whole. Only recently has limited attention been given to study of GTR with respect to composition (Geiger et al. 2012, 132
Willis et al. 2013). ASTM E1131 compositional analysis was employed by (Willis et al. 2013), however, for the most part this study appeared to focus primarily on bulk GTR properties with only limited discussion of total polymer content. A more thorough evaluation the effects of GTR polymer content and chemical composition was reported by (Geiger et al. 2012). Using GTR compositional data determined by ASTM D297, Geiger et al. (2012) studied the relationship of composition of 23 different GTR sources, determined in accordance with ASTM 297, to physical properties of GTR modified asphalt binders to include: softening point, dynamic viscosity and storage stability. Compositional data was employed in development of a compatibility factor ($CF$) calculated as:

$$CF = \frac{\text{polyisoprene}}{\text{(acetone extract + ash)}}$$  \hspace{1cm} (5.1)

It was reported higher poly(isoprene) (NR) content, at least 25 weight percent and a compatibility factor, greater than 1.5, in blends of 15% GTR modified asphalt binders resulted in the most suitable quality GTR modified binders. According to additional asphalt mixture mechanical test results, Geiger et al. (2012) also concluded that the 15% GTR modified binder performed on a similar level to conventional polymer modified asphalt binders. NR is the primary source of poly(isoprene) in tire compounds, therefore, data developed from the proposed method as presented in Table 5.5 can be used to calculate the $CF$ of GTR used in formulation of GTR modified asphalt binders.
5.6.3 Mix Design

Effective asphalt binder content is an important factor in volumetric design of asphalt mixtures. Common knowledge is that excess binder content may lead to mixtures susceptible to permanent deformation while insufficient binder content can be a cause of premature cracking; the latter of which has been of concern in pavements designed with GTR modified asphalt binders. Synonymous to excess binder is excess filler content in asphalt mixtures as excess filler may also yield mixtures susceptible to permanent deformation. A common practice in specification and design of asphalt mixtures containing GTR modified asphalt binders is to arbitrarily increase design binder content by as much as 0.2 to 0.3% to address concerns of lean mixtures and subsequent early cracking.

Data generated from the proposed method can be effectively employed in justification of increasing binder content in mixtures containing GTR modified asphalt binders. From Table 5.5 and FLDOT specifications, it can be seen that the typical functional polymer content of GTR is in the range of 40 to 55%, therefore, it is obvious that the remaining acetone extract, carbon black and ash are neither polymer nor asphalt. With this in mind the specification minimum functional polymer content of 40 % can be utilized to calculate the necessary increase in binder content required to meet volumetric demand.

For example, a design binder content of 5%, designed with conventional binder, substituting GTR modified asphalt binder with a 10% GTR loading level would require an increase in binder content of 0.3%. In other words, 5% asphalt binder with 10% GTR modification with GTR having 40% functional polymer would yield only 94% effective
binder in the GTR modified binder, therefore, in order to ensure 5% binder in the mixture the total binder should be increased to 5.32%.

Similar logic can be employed with respect to filler content as carbon black and ash precursors will more than likely have an effect on the mixtures dust to binder ratio. For example, if a mix contained 6% fines, in the same mixture designed with 5% conventional binder, the non-polymer portion of the rubber in the binder described above would add 0.3% non-binder material to the asphalt mixture increasing the fines to 6.3%. The same mixture designed for 5% binder content with the suggested increased binder content of 0.3 would now contain 5% binder and 6.3% fines. The dust to binder ratio of 6:5 for the conventional binder design is actually 6.3:4.7. Increasing the design binder produced a dust to binder ratio of 6.3:5. Depending on design criteria this change may or may not require an adjustment to the fines content of the mix design coming from aggregate stock piles.

5.8 TGA Summary

TGA is a simple, efficient instrumental method for compositional analysis of GTR used in modification of asphalt binders to be used in production of asphalt paving mixtures. Through TGA analysis of GTR it is possible to determine total functional polymer available in GTR as an asphalt binder modifier, as well as the chemical make-up of the available polymer with respect to content of NR and SBR. Additionally, determination of non-polymer components in GTR is possible, enabling consideration of GTR performance with respect to total composition opposed to bulk physical characteristics. This method has applicability to specification compliance and
formulation of GTR modified asphalt binders, as well as implications in volumetric mixture design for pavement construction.

Several researchers are investigating a variety of issues (e.g. optimal temperatures and blending times) for purposes of making improved performance binders incorporating GTR. Ultimately, a pre-screening process for base materials (i.e. bituminous materials and GTR functional polymer) might be useful as it could help determine compatibility and required polymer loading.
CHAPTER 6
BINDER MODIFICATION

6.1 Overview of Binder Modification

Key findings of this chapter have been published in the proceedings of the 5th International Transport Conference, Wuppertal, Germany, (Baumgardner and Anderson 2008). Processing and optimization of GTR modified asphalt binder formulations were accomplished in four evaluation phases to determine effects on binder properties:

- Phase I - GTR loading;
- Phase II - Processing temperature;
- Phase III - GTR particle size;
- Phase IV - Base asphalt source.

6.2 Materials Utilized for Binder Modification

Asphalt cements and binders used in the work of this chapter have been previously described in Chapter 3, Section 3.2. Asphalt cement number 1, LO PG 64-22 was utilized for work in Phases I to III to prepared GTR and GTR/TOR binders also described in Chapter 3, Section 3.2. Binders 2 to 6 of Chapter 3, Section 2, consist of the six additional asphalt cements to LO PG 64-22 utilized in work of Phase IV. For reference purposes, Table 6.1 list the asphalt cements selected for this chapter. Binders
reheated for subsequent testing were heated to the optimum processing temperature and agitated with 200 rpm low shear agitation for one (1) hour.

Table 6.1
Asphalt Cements Selected

<table>
<thead>
<tr>
<th>Asphalt Cement</th>
<th>Grade</th>
<th>ID</th>
<th>Supplier Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lion Oil Company</td>
<td>PG64-22</td>
<td>LO</td>
<td>El Dorado, Arkansas</td>
</tr>
<tr>
<td>2. Exxon Mobil</td>
<td>PG64-16</td>
<td>EM</td>
<td>Billings, Montana</td>
</tr>
<tr>
<td>3. San Joaquin</td>
<td>AR 4000 (PG64-10)</td>
<td>SJR</td>
<td>Bakersfield, California</td>
</tr>
<tr>
<td>4. Shell</td>
<td>AR 4000 (PG64-10)</td>
<td>SO</td>
<td>Martinez, California</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>50-70 dmm (PG64-)</td>
<td>NS</td>
<td>Sweden</td>
</tr>
<tr>
<td>6. Total</td>
<td>50-70 dmm (PG64-)</td>
<td>TB</td>
<td>France</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>50-70 dmm (PG64-)</td>
<td>OP</td>
<td>Poland</td>
</tr>
</tbody>
</table>

6.3 Phase I - GTR Loadings

LO PG 64-22 binder was modified with loadings of 5.0, 7.5 and 10.0% 850µm (20 mesh) GTR, from ambient ground whole tire rubber supplied by Polyvulc, Inc. of Vicksburg, Mississippi. Additionally, identical loadings of 850µm (20 mesh) GTR were processed in LO PG 64-22 with incorporation of 4.5% Vestenamer 8012 trans-poly(octenamer) reactive polymer (TOR) added based on the weight of rubber in each formulation. Processing of each binder formulation was 200 rpm low shear agitation at 160°C (320°F), as recommended by the TOR supplier, for two (2) hours.

As elemental sulfur is sometimes used to improve the interaction of polymers used in modified asphalt binders, and the TOR was claimed to be reactive with sulfur, an additional modified binder was produced with the Lion Oil PG 64-22 modified with 0.45% TOR and 10.0% 850µm (20 mesh) GTR processed at 160°C with post addition of
0.1% elemental sulfur in order to observe the effect of elemental sulfur on TOR/GTR modified asphalt binders.

Typically, addition of elemental sulfur to polymer modified asphalt binders containing polymers with unsaturated C-C double bonds improves the separation characteristics of the polymer modified asphalt binder. In the case of the GTR/TOR modified binder tested the separation was not improved and was in fact the same or slightly worse, which might indicate that the separation is not a result of polymer separation, but settlement of non-polymeric materials contained in the GTR.

Table 6.2
Dynamic Shear Rheology (DSR) Data as a Function of GTR Content

<table>
<thead>
<tr>
<th>Asphalt Binder Formulation</th>
<th>(G*/\sin\delta) (Original)</th>
<th>(G*/\sin\delta) (RTFO)</th>
<th>(G*/\sin\delta) (PAV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70°C</td>
<td>76°C</td>
<td>82°C</td>
</tr>
<tr>
<td>10. LO 5.0% GTR</td>
<td>0.85</td>
<td>0.49</td>
<td>1.42</td>
</tr>
<tr>
<td>11. LO 7.5% GTR</td>
<td>1.38</td>
<td>0.77</td>
<td>2.32</td>
</tr>
<tr>
<td>12. LO 10.0% GTR</td>
<td>1.51</td>
<td>0.83</td>
<td>2.52</td>
</tr>
<tr>
<td>13. LO 5.0% GTR/TOR</td>
<td>1.08</td>
<td>0.57</td>
<td>2.33</td>
</tr>
<tr>
<td>14. LO 7.5% GTR/TOR</td>
<td>1.76</td>
<td>0.97</td>
<td>2.59</td>
</tr>
<tr>
<td>15. LO 10.0% GTR/TOR</td>
<td>1.92</td>
<td>1.05</td>
<td>3.12</td>
</tr>
<tr>
<td>16. LO 10.0% GTR/TOR plus 0.1% Elemental Sulfur</td>
<td>1.23</td>
<td>0.70</td>
<td>2.63</td>
</tr>
</tbody>
</table>

6.3.1 Dynamic Shear Rheology (DSR) 2 mm Gap Testing of Original Binder

The standard DSR test gap for paving asphalt binders according AASHTO M320 is 1 mm. AASHTO T315 requires that particles within the asphalt be no larger than 0.25 mm, or one quarter of the total gap. GTR is not totally soluble in asphalt and the 850μm (20 mesh) GTR used in this study is more than four (4) times the minimum particle
specified by T315, in addition, 850μm GTR contains some particles larger than 850μm. All of these factors can cause inaccurate DSR test results. Therefore, additional DSR testing on the original binder was performed with a 2mm test gap to evaluate the effects of particle size on test results. Original DSR and phase angle results of 2mm gap testing are given in Table 6.3.

Table 6.3
DSR Test Data – 2 mm vs 1 mm Gap
(25 mm Diameter Geometry)

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>2 mm Gap</th>
<th></th>
<th>1 mm Gap</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70°C</td>
<td>76°C</td>
<td>82°C</td>
<td>70°C</td>
</tr>
<tr>
<td>10. LO 5.0% GTR</td>
<td>0.92</td>
<td>0.56</td>
<td>0.85</td>
<td>0.49</td>
</tr>
<tr>
<td>11. LO 7.5% GTR</td>
<td>1.44</td>
<td>0.83</td>
<td>0.53</td>
<td>1.38</td>
</tr>
<tr>
<td>12. LO 10.0% GTR</td>
<td>1.62</td>
<td>0.95</td>
<td>1.51</td>
<td>0.83</td>
</tr>
<tr>
<td>13. LO 5.0% GTR/TOR</td>
<td>1.24</td>
<td>0.66</td>
<td>1.08</td>
<td>0.57</td>
</tr>
<tr>
<td>14. LO 7.5% GTR/TOR</td>
<td>1.75</td>
<td>0.95</td>
<td>0.53</td>
<td>1.76</td>
</tr>
<tr>
<td>15. LO 10.0% GTR/TOR</td>
<td>2.16</td>
<td>1.17</td>
<td>0.65</td>
<td>1.92</td>
</tr>
<tr>
<td>16. LO 10.0% GTR/TOR Plus 0.1% Elemental Sulfur</td>
<td>1.91</td>
<td>1.04</td>
<td>0.58</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 6.4
Bending Beam Rheology (BBR) / Rotational Viscosity Data as a Function of GTR Content

<table>
<thead>
<tr>
<th>Base Asphalt Binder</th>
<th>S(60) (PAV)</th>
<th>m(60) (PAV)</th>
<th>Rotational Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-12°C</td>
<td>-12°C</td>
<td>135°C</td>
</tr>
<tr>
<td>10. LO 5.0% GTR</td>
<td>221</td>
<td>0.309</td>
<td>872</td>
</tr>
<tr>
<td>11. LO 7.5% GTR</td>
<td>231</td>
<td>0.305</td>
<td>1122</td>
</tr>
<tr>
<td>12. LO 10.0% GTR</td>
<td>191</td>
<td>0.310</td>
<td>1745</td>
</tr>
<tr>
<td>13. LO 5.0% GTR/TOR</td>
<td>245</td>
<td>0.310</td>
<td>814</td>
</tr>
<tr>
<td>14. LO 7.5% GTR/TOR</td>
<td>239</td>
<td>0.304</td>
<td>1180</td>
</tr>
<tr>
<td>15. LO 10.0% GTR/TOR</td>
<td>201</td>
<td>0.316</td>
<td>1620</td>
</tr>
<tr>
<td>16. LO 10.0% GTR/TOR plus 0.1% Elemental Sulfur</td>
<td>192</td>
<td>0.325</td>
<td>1680</td>
</tr>
</tbody>
</table>
Table 6.5

Elastic Recovery / True Grade Data
as a Function of GTR Content

<table>
<thead>
<tr>
<th>Modified Asphalt Binder</th>
<th>Elastic Recovery (%)</th>
<th>Separation (°C)</th>
<th>True Grade</th>
<th>True Grade Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>10. LO 5.0% GTR</td>
<td>45.1</td>
<td>2.8</td>
<td>67.5</td>
<td>-21.9</td>
</tr>
<tr>
<td>11. LO 7.5% GTR</td>
<td>58.3</td>
<td>2.9</td>
<td>70.7</td>
<td>-22.8</td>
</tr>
<tr>
<td>12. LO 10.0% GTR</td>
<td>63.2</td>
<td>5.1</td>
<td>71.6</td>
<td>-22.7</td>
</tr>
<tr>
<td>13. LO 5.0% GTR/TOR</td>
<td>42.5</td>
<td>2.5</td>
<td>70.5</td>
<td>-22.7</td>
</tr>
<tr>
<td>14. LO 7.5% GTR/TOR</td>
<td>57.5</td>
<td>3.6</td>
<td>71.5</td>
<td>-23.6</td>
</tr>
<tr>
<td>15. LO 10.0% GTR/TOR</td>
<td>65.0</td>
<td>4.7</td>
<td>73.2</td>
<td>-22.6</td>
</tr>
<tr>
<td>16. LO 10.0% GTR/TOR + 0.1% Elemental Sulfur</td>
<td>58.5</td>
<td>7.5</td>
<td>71.8</td>
<td>-21.8</td>
</tr>
</tbody>
</table>

6.4 Phase II - Processing Temperature Optimization

Processing parameters to determine optimum processing temperatures, utilizing LO 10.0% GTR/TOR (binder 15) were: 200 rpm low shear agitation for two (2) hours at 160°C (320°F), 177°C (350°F), 193°C (380°F) and 210°C (410°F). An 850μm (20 mesh) particle GTR was used for processing temperature evaluation. Testing was performed in accordance with methods in Chapter 4, Table 4.1, results of temperature optimization binder testing are given in Tables 6.4, 6.7 and 6.8. From the data presented, the optimum processing temperature for evaluation purposes was determined to be 210°C (410°F). Elastic recovery (ER) and phase angle (δ) were the primary determining factors as most other data was very similar. As is shown in Table 6.8 the elastic recovery improved considerably, with an increase in recovery from 50% to 65%, with the increase in temperature from 120°C (320°F) to 193°C (380°F). Elastic recovery values of 68% at 210°C (410°F) were only slightly better than 193°C (380°F).
Table 6.6
Dynamic Shear Rheology (DSR) Data as a Function of Processing Temperature

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>G*/sinδ (Original) 70°C</th>
<th>76°C</th>
<th>82°C</th>
<th>G*/sinδ (RTFOT) 70°C</th>
<th>76°C</th>
<th>82°C</th>
<th>G*/sinδ (PAV) 25°C</th>
<th>22°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160°C</td>
<td>2.45</td>
<td>1.27</td>
<td>0.68</td>
<td>2.26</td>
<td>1.26</td>
<td></td>
<td>4.01</td>
<td>5.88</td>
</tr>
<tr>
<td>177°C</td>
<td>2.51</td>
<td>1.30</td>
<td>0.73</td>
<td>2.31</td>
<td>1.27</td>
<td></td>
<td>3.75</td>
<td>5.48</td>
</tr>
<tr>
<td>193°C</td>
<td>2.18</td>
<td>1.17</td>
<td>0.64</td>
<td>3.71</td>
<td>2.05</td>
<td></td>
<td>3.81</td>
<td>5.57</td>
</tr>
<tr>
<td>210°C</td>
<td>1.91</td>
<td>1.04</td>
<td>0.60</td>
<td>3.10</td>
<td>1.71</td>
<td></td>
<td>3.41</td>
<td>5.03</td>
</tr>
</tbody>
</table>

Table 6.7
Bending Beam Rheology (BBR) / Rotational Viscosity Data as a Function of Processing Temperature

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>S(60) (PAV)</th>
<th>m(60) (PAV)</th>
<th>Rotational Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-12°C</td>
<td>-18°C</td>
<td>-12°C</td>
</tr>
<tr>
<td>Process Temp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160°C</td>
<td>157</td>
<td>360</td>
<td>0.322</td>
</tr>
<tr>
<td>177°C</td>
<td>158</td>
<td>349</td>
<td>0.320</td>
</tr>
<tr>
<td>193°C</td>
<td>182</td>
<td>356</td>
<td>0.317</td>
</tr>
<tr>
<td>210°C</td>
<td>176</td>
<td>237</td>
<td>0.322</td>
</tr>
</tbody>
</table>

Table 6.8
Elastic Recovery / Separation / True Grade Data as a Function of Processing Temperature

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Elastic Recovery (%)</th>
<th>Separation (°C)</th>
<th>True Grade</th>
<th>True Grade Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>50</td>
<td>13.1</td>
<td>76.3</td>
<td>-24.1</td>
</tr>
<tr>
<td>177°C</td>
<td>60</td>
<td>12.6</td>
<td>76.5</td>
<td>-23.9</td>
</tr>
<tr>
<td>193°C</td>
<td>65</td>
<td>15.5</td>
<td>75.3</td>
<td>-23.8</td>
</tr>
<tr>
<td>210°C</td>
<td>68</td>
<td>9.8</td>
<td>73.5</td>
<td>-24.5</td>
</tr>
</tbody>
</table>
Superpave Plus specifications are common in the industry; often a maximum phase angle (δ) will be specified to ensure binders are modified adequately. The phase angle may or may not represent the degree of binder modification; it is however a good indicator of binder curing or that binders have been sufficiently processed. From Figure 6.1, a comparison of the original DSR phase angle versus processing temperature, one can see how phase angle can be used to determine an optimum processing temperature range. This figure indicates that phase angle is considerably dependent on processing temperature and GTR particle size as the higher processing temperatures and the smaller GTR produce lower phase angles.

![Figure 6.1: Original DSR G*/sinδ Phase Angle (δ) vs. Processing Temperature](image)

Figure 6.1

Original DSR G*/sinδ Phase Angle (δ) vs. Processing Temperature
Though 210°C (410°F), selected form ER and phase angle, was used throughout the remaining evaluations, a range of 193°C (380°F) to 210°C (410°F) would be acceptable for processing TOR/GTR modified binders. It may be possible to reduce the two (2) hour processing time used at 210°C (410°F) and 193°C (380°F) to one (1) hour as these asphalt binder/TOR/GTR blends appeared homogeneous after one hour of 200 rpm low shear agitation. For processing at the lower temperatures, two (2) hour processing or more is necessary, which may be a factor of binder/GTR compatibility. It is important to note that the common practice for preparation of Styrene-Butadiene-Styrene (SBS) modified asphalt binders is to employ a processing temperature range of 180°C (356°F) to 200°C (392°F); this may as well be the acceptable processing temperature range for TOR/GTR modified asphalt binders.

An important observation in the temperature optimization evaluation was the tendency for the 850μm (20 mesh) GTR modified binders to profusely creep out of the rolling thin film oven (RTFO) test bottles. Estimates were that approximately half of the contents crept out during the RTFO aging procedure. This important factor was considered in GTR particle size optimization evaluations presented in Section 6.5.

6.5  Phase III - Ground Tire Rubber (GTR) Particle Size Optimization

The optimal temperature determined in the temperature optimization study using 850μm (20 mesh) GTR was extended to formulations with GTR having particle sizes of 600μm and 250μm (30 and 60 mesh), binder numbers 17 to 20 respectively, utilizing the same processing parameters of 200 rpm low shear agitation for two (2) hours. Binders for GTR particle size optimization using the optimized processing temperature were
prepared and tested in accordance with methods in Chapter 4, Table 4.1. Results of binder testing for GTR particle size optimization are given in Tables 6.9, 6.10 and 6.11.

Table 6.9
Dynamic Shear Rheology (DSR) Data as a Function of GTR Particle Size

<table>
<thead>
<tr>
<th>GTR Particle Size</th>
<th>G*/sinδ (Original) 70°C</th>
<th>G*/sinδ (Original) 76°C</th>
<th>G*/sinδ (Original) 82°C</th>
<th>G*/sinδ (RTFO) 70°C</th>
<th>G*/sinδ (RTFO) 76°C</th>
<th>G*/sinδ (RTFO) 82°C</th>
<th>G*sinδ (PAV) 25°C</th>
<th>G*sinδ (PAV) 22°C</th>
<th>G*sinδ (PAV) 19°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>850μm</td>
<td>1.91</td>
<td>1.04</td>
<td>0.60</td>
<td>3.10</td>
<td>1.71</td>
<td>3.41</td>
<td>5.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600μm</td>
<td>1.63</td>
<td>0.94</td>
<td>0.54</td>
<td>2.43</td>
<td>1.33</td>
<td>4.82</td>
<td>7.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250μm</td>
<td>1.75</td>
<td>0.95</td>
<td>0.55</td>
<td>2.53</td>
<td>1.44</td>
<td>4.36</td>
<td>6.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.10
Bending Beam Rheology (BBR) / Rotational Viscosity Data as a Function of GTR Particle Size

<table>
<thead>
<tr>
<th>GTR Particle Size</th>
<th>Elastic Recovery (%)</th>
<th>Separation (°C)</th>
<th>True Grade Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>850μm</td>
<td>68</td>
<td>9.8</td>
<td>73.5 -24.5 98.0</td>
</tr>
<tr>
<td>600μm</td>
<td>65</td>
<td>11.8</td>
<td>71.0 -26.2 97.2</td>
</tr>
<tr>
<td>250μm</td>
<td>68</td>
<td>8.9</td>
<td>71.4 -26.6 98.0</td>
</tr>
</tbody>
</table>

Table 6.11
Elastic Recovery / Separation / True Grade Data as a Function of GTR Particle Size

<table>
<thead>
<tr>
<th>GTR Particle Size</th>
<th>S(60) (PAV) -12°C</th>
<th>m(60) (PAV) -12°C</th>
<th>Rotational Viscosity (149°C) (163°C) (177°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>850μm</td>
<td>176</td>
<td>0.322</td>
<td>1,020 568 393</td>
</tr>
<tr>
<td>600μm</td>
<td>143</td>
<td>0.339</td>
<td>1,140 710 440</td>
</tr>
<tr>
<td>250μm</td>
<td>126</td>
<td>0.357</td>
<td>1,120 632 483</td>
</tr>
</tbody>
</table>
As with temperature optimization, elastic recovery was used as the primary determining factor for optimization of ground tire rubber particle size. The 250μm (60 mesh) crumb rubber modified binder performed best and did not creep out of the RTFO bottles as did the 850μm and 600μm (20 and 30 mesh) materials. While some of the other test results are actually lower than those with the 600μm (30 mesh) material, the 250μm (60 mesh) material actually produced a more homogeneous material with a better appearance than the 850μm and 600μm (20 or 30 mesh) materials. The 250μm (60 mesh) TOR/GTR modified binder was more homogeneous and behaved more as one product than a mixture of two products. Based on these results, a range of 600μm (30 mesh) to 250μm (60 mesh) or particle size of no greater than 600μm (30 mesh) GTR may be more suitable for TOR/GTR asphalt binder modification.

6.6 Phase IV - Binder Evaluation

The asphalt cements identified in Table 6.1 were modified with TOR and 250μm (60 mesh) GTR processed at 210°C (410°F). Table 6.12 presents the binder formulation used for each of these binders.

Table 6.12

Binder Evaluation Formulation

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>PRODUCT</th>
<th>WEIGHT %</th>
<th>SG</th>
<th>VOLUME %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE ASPHALT</td>
<td>Asphalt Binder</td>
<td>89.55</td>
<td>1.02</td>
<td>88.88</td>
</tr>
<tr>
<td>TOR ADDITIVE</td>
<td>Degussa 8012</td>
<td>0.45</td>
<td>0.98</td>
<td>0.47</td>
</tr>
<tr>
<td>GTR</td>
<td>Polyyule PV0060</td>
<td>10.00</td>
<td>0.95</td>
<td>10.66</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>100.00</td>
<td>98.78</td>
<td>100.00</td>
</tr>
</tbody>
</table>
These binders were tested in accordance with methods in Chapter 4, Table 4.1. Results of binder testing are given in Tables 6.13, 6.14 and 6.15.

Table 6.13

Dynamic Shear Rheology (DSR) Data as a Function of Base Asphalt Cement

<table>
<thead>
<tr>
<th>Base Asphalt Cement</th>
<th>G*/sinδ (Original)</th>
<th>G*/sinδ (RTFO)</th>
<th>G*sinδ (PAV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70°C</td>
<td>76°C</td>
<td>82°C</td>
</tr>
<tr>
<td>1. Lion Oil</td>
<td>1.75</td>
<td>0.95</td>
<td>0.55</td>
</tr>
<tr>
<td>2. ExxonMobil</td>
<td>2.45</td>
<td>1.35</td>
<td>0.77</td>
</tr>
<tr>
<td>3. SJR</td>
<td>1.31</td>
<td>0.71</td>
<td>0.41</td>
</tr>
<tr>
<td>4. Shell</td>
<td>1.34</td>
<td>0.75</td>
<td>0.42</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>2.52</td>
<td>1.41</td>
<td>0.81</td>
</tr>
<tr>
<td>6. Total</td>
<td>2.46</td>
<td>1.37</td>
<td>0.78</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>3.18</td>
<td>1.75</td>
<td>0.97</td>
</tr>
</tbody>
</table>

As previously stated, the standard DSR test gap for paving asphalt binders according AASHTO M320 is 1mm, Table 6.14 presents the 1mm and 2mm data for the TOR/GTR modified binders tested in the binder evaluations. While the 250μm (60 mesh) GTR meets the requirements of AASHTO T315 for the 1mm gap, the recommended range of 600 - 250μm (30 – 60 mesh) might necessitate the 2mm test gap. Figure 6.2 presents a comparison of original DSR G*/sinδ values for both the 1mm and 2mm testing for all binders and the Lion Oil optimization formulations. Of importance is that the outliers are all from the group of 850μm (20 mesh) modified binders, which is an indication of the confounding effects of particles too large for the test gap employed.
Table 6.14

DSR Test Data – 2 mm vs 1 mm Gap (25 mm Geometry)

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>2 mm Gap</th>
<th></th>
<th></th>
<th>1 mm Gap</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70°C</td>
<td>76°C</td>
<td>82°C</td>
<td>70°C</td>
<td>76°C</td>
<td>82°C</td>
</tr>
<tr>
<td>15. LO PG 64-22, 850μm, 160°C</td>
<td>2.45</td>
<td>1.27</td>
<td>0.68</td>
<td>1.46</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>15. LO PG 64-22, 850μm, 177°C</td>
<td>2.51</td>
<td>1.30</td>
<td>0.73</td>
<td>1.08</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>15. LO PG 64-22, 850μm, 193°C</td>
<td>2.18</td>
<td>1.17</td>
<td>0.64</td>
<td>1.29</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>17. LO PG 64-22, 850μm, 210°C</td>
<td>1.91</td>
<td>1.04</td>
<td>0.60</td>
<td>1.24</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>18. LO PG 64-22, 600μm, 210°C</td>
<td>1.63</td>
<td>0.94</td>
<td>0.54</td>
<td>1.67</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>19. LO PG 64-22, 250μm, 210°C</td>
<td>1.75</td>
<td>0.95</td>
<td>0.55</td>
<td>1.70</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>20. EM PG 64-16, 250μm, 210°C</td>
<td>2.45</td>
<td>1.35</td>
<td>0.77</td>
<td>1.26</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>21. SIR PG 64-10, 250μm, 210°C</td>
<td>1.31</td>
<td>0.71</td>
<td>0.41</td>
<td>1.23</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>22. SO PG 64-10, 250μm, 210°C</td>
<td>1.34</td>
<td>0.75</td>
<td>0.42</td>
<td>1.24</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>23. NS PG 64-22, 250μm, 210°C</td>
<td>2.52</td>
<td>1.41</td>
<td>0.81</td>
<td>1.37</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>24. TB PG 64-22, 250μm, 210°C</td>
<td>2.46</td>
<td>1.37</td>
<td>0.78</td>
<td>1.36</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>25. OP PG 64-22, 250μm, 210°C</td>
<td>3.18</td>
<td>1.75</td>
<td>0.97</td>
<td>1.61</td>
<td>0.96</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.2

Comparison of Original Binder G*/sinδ for 1 mm and 2 mm Gap
Figure 6.3 presents a comparison of original DSR phase angle to processing temperature similar the comparison presented in Figure 6.1 with the exception that these data are for the different binders all modified with 250μm (60 mesh) GTR. The typical phase angle maximum for PG-Plus specifications is 75°. The target grade for the 10% TOR/GTR modified binders is PG 76-22, from Figure 6.3 it is realized that 10% GTR is not sufficient for most of the binders tested, it is expected that loadings near 12% may be more appropriate.

![Figure 6.3](image.png)

Figure 6.3

Comparison of Different Binder Original Phase Angle (δ) vs. Processing Temperature
True grade data in table 6.15 reveals that four (4) of the binders had an increase of two (2) PG-grades while three had a PG-grade increase of one (1) PG-grade upon modification with 10% GTR plus TOR. The Orlen 50-70 asphalt had the best performance with a true grade of 79.4-26.0 (PG 76-22) while the San Joaquin Refining (SJR) AR 4000 had the least PG-grade improvement achieving only a true grade of 69.3-18.9 (PG 64-16). These results are typical of those expected with the binders evaluated, greater or lesser grades can be achieved by adjusting the loading of GTR/TOR.

Table 6.15

<table>
<thead>
<tr>
<th>Base Asphalt Binder</th>
<th>Elastic Recovery (%)</th>
<th>Separation (°C)</th>
<th>True Grade</th>
<th>True Grade Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lion Oil</td>
<td>68</td>
<td>8.9</td>
<td>71.4</td>
<td>-26.6</td>
</tr>
<tr>
<td>2. ExxonMobil</td>
<td>73</td>
<td>9.7</td>
<td>77.8</td>
<td>-26.0</td>
</tr>
<tr>
<td>3. SJR</td>
<td>75</td>
<td>13.1</td>
<td>69.3</td>
<td>-18.9</td>
</tr>
<tr>
<td>4. Shell</td>
<td>73</td>
<td>11.6</td>
<td>70.1</td>
<td>-23.9</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>68</td>
<td>10.5</td>
<td>77.3</td>
<td>-28.4</td>
</tr>
<tr>
<td>6. Total</td>
<td>73</td>
<td>9.4</td>
<td>76.9</td>
<td>-27.8</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>70</td>
<td>9.2</td>
<td>79.4</td>
<td>-26.0</td>
</tr>
</tbody>
</table>

True grade ranges are presented in table 6.15 as temperature differential in °C between the upper grading temperature °C and the lower grading temperature °C. For example the Orlen 50-70 modified with 10% GTR plus TOR had a true grade of 79.4-26.0 which yields a true grade range of 105.4 °C.

Separation data are also presented in table 6.15. The tube separation test is often used to measure the separation of polymer from asphalt binder. This test consists of pouring 50 grams of modified asphalt binder into an aluminum tube (toothpaste tube)
which is placed upright in a forced draft oven at 163°C (325°F) for 48 hours. After 48 hours the tube is removed from the oven and cooled, the tube is cut into three equal parts with tests being run on the top and bottom thirds. Typical tests may include G*, G*/sinδ, phase angle and softening point. In the case of softening point as used in this evaluation the softening point (°C) is measured on the top and bottom thirds of the prepared sample and the difference in results from top to bottom are reported in °C. The typical separation specification limit is a maximum of 6 °C difference between top and bottom portion test values. Figure 6.4 presents a relationship between base binder composition and separation. From figure 6.4 and data presented in Table 3.8, Chapter 3, Section 3.2.3, it can be seen that the base binders with lower asphaltene to resin ratios (A/A+R) had greater separation than those binders with higher asphaltene to resin ratios.

![Figure 6.4](image)

Figure 6.4

Separation vs. Asphaltene to Resin Ratio (A/A+R)
Table 6.16 presents BBR data for the seven GTR/TOR modified binders as a function of the base binder. Of importance to note is the affect GTR modification had on low temperature grading. Comparing data presented in Table 6.16 to data presented in Table 3.4 for the original asphalt cements it can be seen that addition of GTR has reduced the stiffness, s-value, as well as improved the m-value at -12°C for all seven binders. This is atypical of modification of most binders with polymers such as SBS and is believed in the case of GTR modification to be due to contribution of lighter oils and lower molecular weight polymers to low temperature properties. However, referring to the PAV results of Table 6.13 it can be seen that the low temperature grade for GTR/TOR modified binders based on asphalt cements 3 and 4 (SJR and SO) remain low temperature grade controlled by the PAV results.
Table 6.16
Bending Beam Rheology / Rotational Viscosity Data

<table>
<thead>
<tr>
<th>Base Asphalt Binder</th>
<th>S(60) (PAV)</th>
<th>m(60) (PAV)</th>
<th>Rotational Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-6°C</td>
<td>-12°C</td>
<td>-18°C</td>
</tr>
<tr>
<td>1. Lion Oil</td>
<td>126</td>
<td>273</td>
<td>0.357</td>
</tr>
<tr>
<td>2. ExxonMobil</td>
<td>119</td>
<td>245</td>
<td>0.333</td>
</tr>
<tr>
<td>3. SJR</td>
<td>181</td>
<td>407</td>
<td>0.390</td>
</tr>
<tr>
<td>4. Shell</td>
<td>228</td>
<td>456</td>
<td>0.336</td>
</tr>
<tr>
<td>5. Nynas</td>
<td>283</td>
<td>552</td>
<td>0.309</td>
</tr>
<tr>
<td>6. Total</td>
<td>126</td>
<td>273</td>
<td>0.347</td>
</tr>
<tr>
<td>7. Orlen</td>
<td>106</td>
<td>212</td>
<td>0.318</td>
</tr>
</tbody>
</table>
6.7 Summary and Key Binder Modification Findings

GTR and GTR/GTR formulations with Lion Oil PG 64-22 indicated the target GTR loading to achieve an AASHTO M320 PG76-22 grade modified binder would be approximately 10% with GTR/TOR and slightly higher with GTR alone. Since ground tire rubber may also contain carbon black, silica and other ingredients which were compounded into the rubber that are still present, it is generally believed, and was shown in Chapter 5, that approximately 30% functional polymeric material remains in ground tire rubber; therefore, modification with 10% ground tire rubber is comparable to modification with approximately 3% of a styrene-butadiene-styrene (SBS) block copolymer depending on molecular configuration and weight. Addition of TOR seemed to increase binder stiffness slightly and is typical of most wax like additives used to modify asphalt cements, however, increased stiffness was considered to be minimal and GTR vs GTR/TOR results were considered to be the same in practice only requiring slight adjustments in modifier loading to achieve comparable binder properties.

There was no improvement in separation results due to addition of TOR as had been reported by the TOR supplier. Separation test data are considered to indicate that most separation with the TOR/GTR modified binders may be due to the non-polymeric materials contained in the GTR and not from separation of polymer.

The TOR supplier recommended processing temperature of 160°C (320°F) was determined to be too low; therefore, processing temperature evaluations were performed to optimize processing temperature parameters. Processing temperature evaluations were performed as described and revealed the optimum processing temperature for blending Lion Oil PG 64-22 with 10% 20 mesh (850μm) ground tire rubber 0.45% TOR, two (2)
hours at 200 rpm low shear paddle agitation, to be 410°F (210°C). Elastic recovery (ER) and phase angle were the primary determining factors as most other data was very similar. As shown, the elastic recovery improved considerably, with an increase in recovery from 50% to 65%, with the increase in temperature from 320°F (120°C) to 380°F (193°C). Elastic recovery values at 410°F (210°C) were only slightly better than 380°F (193°C). Therefore a range of 380°F (193°C) to 410°F (210°C) would be recommended for processing of GTR formulations. This processing temperature range is similar to the common practice for preparation of Styrene-Butadiene-Styrene (SBS) modified asphalt binders with a processing temperature range of 356°F (180°C) to 392°F (200°C); this as well may be the acceptable processing temperature range for TOR/GTR modified asphalt binders. As with other polymer modified binders, actual storage temperature would be considerably less than the suggested manufacturing temperature range. Storage temperature is expected to be in the 300°F (149°C) to 350°F (177°C) range, typically around 325°F (163°C).

Blends of Lion Oil PG 64-22 were prepared with 30 and 60 mesh (600μm and 250μm) ground tire rubber using 200 rpm low shear paddle agitation at the selected optimum processing temperature of 410°F (210°C). It was observed that the 20 mesh (850μm) ground tire rubber modified binders had a tendency to creep out of the rolling thin film oven (RTFO) test bottles. As in temperature optimization, elastic recovery and phase angle were used as the primary determining factor for optimization of ground tire rubber particle size. The 60 mesh (250μm) crumb rubber modified binder performed best and did not creep out of the RTFO bottles as did the 20 and 30 mesh (850μm and 600μm) materials. While some of the other test results for the 60 mesh (250μm) ground tire
rubber modified formulations are actually lower than those with the 30 mesh (600μm) material, the 60 mesh (250μm) material actually produced a more homogeneous material with a better appearance than the 20 or 30 mesh (850μm and 600μm) materials. The 60 mesh (250μm) ground tire rubber modified binder was more homogeneous and behaved more as one product than a mixture of two products. Based on results of GTR particle size evaluations a range of 30 (600μm) to 60 mesh (250μm) ground tire rubber may be most suitable for GTR modified asphalt formulations.

Evaluation of modified asphalt binder formulations with various binders from a number of crude sources revealed that quality asphalt paving binders can be produced by co-modification with GTR and TOR. Observations are that GTR/TOR modified asphalt binders have similar characteristics to conventional polymer modified asphalt binders and that the effect of binder source and binder chemistry is also similar. Modification of asphalt binders with GTR/TOR combinations is a viable method of binder modification and can produce performance grade binders that perform as well as conventional polymer modified asphalt binders with respect to binder physical properties. The difference being that GTR/TOR may contain more total modifier than conventional polymer modified asphalt binders and volumetric adjustments may be necessary in mixtures containing these binders.
CHAPTER 7
GTR MODIFIED BINDER SPECIFICATIONS

7.1 Overview of GTR Modified Binder Specifications

Key findings of this chapter have been published in the Transportation Research Record (Baumgardner and D‘Angelo 2012) and are in a second work submitted for publication consideration (Baumgardner et al. 2016).

Historically, specifications for GTR modified binders in most asphalt paving applications have been recipe or method type, in which a specific process and amounts of material are described to produce a specific product. When contractors have experience with these specifications, good performance can often be achieved (Heitzman 1992, Epps 1994). However, this makes transferring these processes and specifications from one location to another difficult and increases the potential for failures (CalTrans 2005).

Rudimentary test procedures have been attempted to provide some type of quality control for the various processes. The primary device has been the handheld rotational viscometer (Epps 1994). This method can provide some indication of viscosity increase from the addition and blending of GTR into the binder, but it has high variability. Limited testing of GTR modified binders has been conducted with Superpave on GTR particle sizes that can be handled in the 1 or 2 mm gap using the parallel-plate geometries, typically 30 mesh material or smaller (Abdelrahman et al. 1999, Loh et al.
2000, Baumgardner and Anderson 2008). These studies did show the increase in modulus of the binder with addition of GTR and that the size, percentage of rubber, and base asphalt cement all affected the binder properties. However, in general use, GTR comes in many sizes, and the most widely used material is typically larger than 30 mesh. These size variations require testing of the binder with larger particle sizes using geometries with larger gaps. Many studies have shown that GTR size and shape, mixing temperature, and asphalt binder all affect the final properties of the GTR modified binder (Abdelrahman et al. 1999, Loh et al. 2000, CalTrans 2005, Baumgardner and Anderson 2008). Without a well-defined binder specification, adoption of GTR modified binder by U.S. highway agencies will be almost impossible to achieve. Test procedures that can evaluate performance characteristics of GTR modified binder are crucially needed.

7.2 Objective of GTR Modified Binder Specification Efforts

Superpave performance graded (PG) binder specification became the standard used throughout the United States in the mid 1990s, as a result, rheological testing of binders is now a standard practice to evaluate performance characteristics of neat and modified binders. Superpave specifications have limitations that restrict the materials that can be tested. Existing specifications use the DSR and plate–plate (parallel plate) (PP) geometry with a 1 mm gap for testing of binders at high and intermediate temperatures (Petersen 1994). This geometry limits the materials that can be tested between the plates. Particulate matter larger than 250 μm cannot be tested because of the possible interaction of particulate matter on the torque and strain response of the binder (Petersen 1994). Typical GTR modified binder has rubber particles much larger than 250
μm (0.25 mm). GTR particles may range in size from 0.5 mm to more than 1 mm. A 1 mm particle tested with a DSR 1 mm gap PP geometry would touch the top and bottom plates at the same time, so that test results would represent the GTR particle rather than a GTR modified binder.

Performing PG testing on GTR modified binders with larger particles requires using geometries with larger gap sizes. One approach that has been used in the food industry is testing with concentric-cylinder (CC) geometries. DSRs currently used for asphalt testing can be adapted to use a Searle system. In this system the center cylinder (or bob) rotates, and the outside cylinder (or cup) is stationary (Steffe 1996, Schramm 1994). This type of system can perform all the types of testing currently used for asphalt binder grading. The advantage is that the cup and bob (CB) geometry can easily handle gaps from 4 to 7 mm and therefore can accommodate larger GTR particles. One disadvantage is that the system requires a much larger sample for testing (e.g. approximately 32 grams for the CB geometry versus approximately 4 grams for the 2 mm gap PP geometry). Figure 7.1 presents a graphic showing the bob submerged into the cup with GTR modified binder. Figure 7.2 presents a photograph of the CB geometry with the bob extended above the cup.
The objective of the efforts presented in this chapter was to perform the initial evaluation of the CB system for its suitability for asphalt binder testing. A preliminary evaluation was made of the ability of the new CB system to provide results similar to the current PP geometry method. The evaluation was performed by testing neat and
polymer-modified binders. An initial evaluation of the geometry to test GTR modified binders was also conducted to evaluate potential differences in testing with a larger gap size.

7.3 Experimental Plan of GTR Modified Binder Specifications

Testing of the CB geometry was conducted on different rubber sizes and one base binder. Comparisons were made between standard PG grading using AASHTO M320 and MP19 of the control and GTR modified binders with parallel-plate geometry with 1 and 2 mm gaps and the CB geometry with a 6.5 mm gap. MSCR testing (AASHTO MP19) was also evaluated with the same materials and DSR geometries. A PG 64-22 was blended with 20, 30, and 60 mesh rubber particles at different percentages. Table 7.1 shows the full testing plan. All GTR was ambient grind; gradations are shown in Table 7.2.
Table 7.1

Test for Binders and Geometries

<table>
<thead>
<tr>
<th>Binder type</th>
<th>Geometry and Gap Size</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PP1</td>
<td>PP2</td>
<td>CB6.5</td>
</tr>
<tr>
<td>1. PG 64-22</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>25. PG 70-22</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>26. PG 76-22</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>27. PG 64-22 10% 60M</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>28. PG 64-22 15% 60M</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>29. PG 64-22 10% 30M</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>30. PG 64-22 15% 30M</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>31. PG 64-22 15% 20M</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>32. PG 64-22 20% 20M</td>
<td></td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
<td>M 320, MP19</td>
</tr>
<tr>
<td>34. PG 64-34</td>
<td></td>
<td>MP19</td>
<td></td>
<td>MP19</td>
</tr>
</tbody>
</table>

Table 7.2

Sieve Analysis of GTR Sizes

<table>
<thead>
<tr>
<th>Percent Passing</th>
<th>Liberty 20 Mesh</th>
<th>PolyVulc 30 Mesh</th>
<th>PolyVulc</th>
<th>PolyVulc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PLB2B5044</td>
<td>PLB5E5250</td>
<td>PLB4D486</td>
<td>PLB4D2023</td>
</tr>
<tr>
<td>10 (2000 micron)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>20 (850 Micron)</td>
<td>58.89</td>
<td>99.84</td>
<td>97.91</td>
<td></td>
</tr>
<tr>
<td>30 (600 Micron)</td>
<td>7.05</td>
<td>97.51</td>
<td>94.78</td>
<td></td>
</tr>
<tr>
<td>40 (425 Micron)</td>
<td>0.72</td>
<td>54.9</td>
<td>62.97</td>
<td></td>
</tr>
<tr>
<td>50 (300 Micron)</td>
<td>0.64</td>
<td>27.21</td>
<td>31.97</td>
<td>99.83</td>
</tr>
<tr>
<td>80 (180 Micron)</td>
<td>0.4</td>
<td>8.27</td>
<td>7.3</td>
<td>67.07</td>
</tr>
<tr>
<td>100 (150 Micron)</td>
<td></td>
<td></td>
<td></td>
<td>41.63</td>
</tr>
<tr>
<td>200 (7.5 Micron)</td>
<td></td>
<td></td>
<td></td>
<td>7.4</td>
</tr>
</tbody>
</table>
It was originally believed there was a large difference between the 30 and 60 mesh GTR; however, a sieve analysis of the rubber showed that the 60 mesh was only slightly finer than the 30 mesh.

An Anton Paar Smart Pave 101 DSR was used for the high and intermediate testing required for AASHTO M320 and MP19. Rolling thin-film oven (RTFO) testing of the binders was conducted with standard 25 mm diameter plates with 1 and 2 mm gaps. The CB geometry used a 27 mm cup and a 14 mm bob, which produced a 6.5 mm gap. Intermediate temperature testing was conducted with 8 mm diameter plates with a 2 mm gap according to standard T315 test procedures. Testing of larger GTR at intermediate temperatures was part of further evaluations to determine if the CB geometry can be used at intermediate temperatures. Standard BBR molds (6.35 by 12.7 mm) were used for all low-temperature testing because it was believed they could accommodate GTR up to 1 mm in size without adversely affecting the test results.

The initial evaluation compared results of the PP geometry with the CB geometry. Replicate tests were not performed for the initial evaluation. The two geometries were compared by evaluating any difference in results against the single-operator precision d2s of the current AASHTO T315 procedure. This initial evaluation was used to determine if the new geometry would provide results that are currently accepted in the asphalt industry. Future development of full test procedures is envisioned to include a thorough statistical evaluation of the reputability and reproducibility of the new geometries. Shear stress ($\tau$) and shear strain ($\gamma$) calculations for the CB shown in Equations 7.1 and 7.2, respectively, differ slightly from the parallel-plate calculations:
Shear Stress = \( \tau = \frac{T}{2\pi hR_b^2} \)  

(7.1)

Shear Strain = \( \gamma = \frac{\theta R_b}{(R_c - R_b)} \)  

(7.2)

Where:

\( T \) = torque

\( h \) = height of the bob

\( R_b \) = radius of the bob

\( R_c \) = radius of the cup

\( \theta \) = angular rotation of the bob

The CB does not require trimming, which is an advantage with GTR modified binders. The actual surfaces that control the geometry are defined by the surface of the bob and the walls of the cup. Similar to the standard PP geometry, in which the stress and strain are controlled by the outside edge, the CB geometry is controlled by the surface area of the bob and the radius of the bob and cup. Any binder at the bottom of the cup and any that overflows the bob have an insignificant effect on the stress and can be ignored.

7.4 Results of GTR Modified Binder Specification Development

Initial evaluation compared test results from standard PP geometry with results from CB for asphalts that can be tested meeting all current specifications. Three binders were evaluated: a neat PG 64-22 from Lion Oil produced from a light Saudi crude stock, a PG 70-22 produced from the Lion 64-22 plus polyphosphoric acid (PPA), and a PG 76-
produced from the PG 70-22 plus 2.25% styrene–butadiene–styrene polymer. There were almost no differences in the M320 test results for both the standard 1 mm and 2 mm gap PP geometry and the 6.5 mm gap CB geometry. The percentage difference between results for the PG 64-22 was zero; for the PG 70-22, it was 4.6%; and for the PG 76-22, it was 8.9%. In each case this was less than the single-operator d2s for DSR RTFO results, which indicates that the new CB geometry provides similar results to the standard 1 mm gap PP geometry. The comparison of high-temperature continuous grades is shown graphically in Figure 7.3. All M320 test results are shown in Table 7.3.

![Figure 7.3](image_url)

Figure 7.3

Continuous High Temperature Grade for Three Typical Binders Tested with Various Geometries
Table 7.3
Superpave M320 Results Using the Three Different Geometries

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Binder Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PG 64-22</td>
</tr>
<tr>
<td>PP 1 mm</td>
<td>Continuous PG grade</td>
</tr>
<tr>
<td></td>
<td>G*/sin δ @ PG grade</td>
</tr>
<tr>
<td>PP 2 mm</td>
<td>Continuous PG grade</td>
</tr>
<tr>
<td></td>
<td>G*/sin δ @ PG grade</td>
</tr>
<tr>
<td>CB 6.5 mm</td>
<td>Continuous PG grade</td>
</tr>
<tr>
<td></td>
<td>G*/sin δ @ PG grade</td>
</tr>
<tr>
<td>% diff</td>
<td>CB/PP-1 mm</td>
</tr>
<tr>
<td>PAV DSR</td>
<td>Continuous PG grade</td>
</tr>
<tr>
<td>BBR S</td>
<td>Continuous PG grade</td>
</tr>
<tr>
<td>Diff S m</td>
<td>°C</td>
</tr>
</tbody>
</table>
The GTR modified binders were tested in the three DSR geometries as appropriate to their particle sizes. The 15% 30 mesh GTR was not tested in the 1 mm gap PP geometry, and the 20 mesh GTR was only tested in the CB 6.5 mm geometry. CB results from the GTR modified binders provided a slightly higher variation from the 1 mm gap PP results than the neat or polymer modified binders. The average difference between the 1 mm gap PP and the CB was 12.5%, with a range of 9.7 to 15.3%. In general, these results indicate that the 1 mm gap PP and CB do not compare within the current single-operator d2s. However, the wide variability of the results may indicate that the issue is not the testing geometry but the material itself, as GTR modified binder with high percentages (10% to 15%) of GTR may make it difficult to get consistent material from sample to sample. Figure 7.4 presents a bar graph of the differences in results from the different geometries and different materials.
Further evaluation of the new testing geometry included running samples using AASHTO MP19 and TP70 MSCR testing. The same binders were used in the MSCR test as in standard PG testing. Control binders provided mixed results as to the acceptability of the CB to replace the 1 mm gap PP. There was only a 4% difference in the MSCR results for the PG 64-22 binder; however, the difference between the results for the PG 70-22 and PG 76-22 binders were significantly higher at 26% and 34%, respectively. To determine if these discrepancies were a geometry problem or a possible testing error, an additional binder was tested. This binder, a PG 64-34, was selected because it was a highly modified material prepared from a soft base asphalt cement.

The PG 64-34 binder provided MSCR results in both geometries very similar to the neat PG 64-22 results. Results for the PG 64-34 are well within the single-operator
d2s for the MSCR test, Figure 7.5. All MSCR data are presented in Table 7.4. It is likely that the PG 76-22 results are an anomaly in that MSCR testing done when the compliance value is well below 0.25 may be highly variable because of limitations of the DSR equipment to accurately measure strain at very low values. The MSCR test is also more sensitive to temperature and polymer modification, which can be seen in higher variability (D’Angelo and Dongre 2009). As for the PG 70-22 results, these need further investigation to determine if sample contamination may have occurred.

![Figure 7.5](image)

Figure 7.5
Statistical Difference between 1 mm Parallel Plate and Cup and Bob Geometry Results for MSCR Compliance at 0.1 kPa and 3.2 kPa for a Highly Modified PG 64-34 Binder

Testing of the GTR modified binder in the CB geometry for MSCR showed differences in comparison with the 1-mm gap PP results. The CB results for the various
GTR modified binders all had lower compliance values than the 1-mm gap PP values in a range of 25% to 35%. Several reasons were investigated for this difference.
Table 7.4
Superpave MP19 Results Using the Three Different Geometries

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Test Temperature</th>
<th>PG 64-22</th>
<th>PG 70-22</th>
<th>PG 76-22</th>
<th>10% 60 mesh</th>
<th>15% 60 mesh</th>
<th>10% 30 mesh</th>
<th>15% 30 mesh</th>
<th>15% 20 mesh</th>
<th>20% 20 mesh</th>
<th>PG 64-34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jnr 0.1 PP 1 mm</td>
<td>64 C</td>
<td>3.207</td>
<td>0.923</td>
<td>0.105</td>
<td>0.591</td>
<td>0.217</td>
<td>0.609</td>
<td></td>
<td></td>
<td></td>
<td>0.270</td>
</tr>
<tr>
<td>Jnr 0.1 PP 2 mm</td>
<td>64 C</td>
<td>2.958</td>
<td>0.848</td>
<td>0.101</td>
<td>0.636</td>
<td>0.203</td>
<td>0.662</td>
<td></td>
<td></td>
<td></td>
<td>0.240</td>
</tr>
<tr>
<td>Jnr 0.1 CB 6.5 mm</td>
<td>64 C</td>
<td>3.143</td>
<td>0.809</td>
<td>0.180</td>
<td>0.711</td>
<td>0.255</td>
<td>0.729</td>
<td></td>
<td></td>
<td></td>
<td>0.289</td>
</tr>
<tr>
<td>% difference</td>
<td></td>
<td>2.0</td>
<td>12.4</td>
<td>71.4</td>
<td>-20.3</td>
<td>-17.5</td>
<td>-9.0</td>
<td>-20.4</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Jnr 3.2 PP 1 mm</td>
<td>64 C</td>
<td>3.407</td>
<td>1.188</td>
<td>0.147</td>
<td>1.050</td>
<td>0.572</td>
<td>1.122</td>
<td></td>
<td></td>
<td></td>
<td>0.301</td>
</tr>
<tr>
<td>Jnr 3.2 PP 2 mm</td>
<td>64 C</td>
<td>3.285</td>
<td>1.160</td>
<td>0.149</td>
<td>1.041</td>
<td>0.516</td>
<td>1.064</td>
<td></td>
<td></td>
<td></td>
<td>0.532</td>
</tr>
<tr>
<td>Jnr 3.2 CB 6.5 mm</td>
<td>64 C</td>
<td>3.266</td>
<td>0.882</td>
<td>0.197</td>
<td>0.854</td>
<td>0.373</td>
<td>0.848</td>
<td></td>
<td></td>
<td></td>
<td>0.273</td>
</tr>
<tr>
<td>% difference</td>
<td></td>
<td>4.0</td>
<td>26</td>
<td>34</td>
<td>19</td>
<td>35</td>
<td>24</td>
<td>25</td>
<td></td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>% change Jnr PP 1 mm</td>
<td>64 C</td>
<td>0.06</td>
<td>0.29</td>
<td>0.40</td>
<td>0.78</td>
<td>1.64</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% change Jnr PP 2 mm</td>
<td>64 C</td>
<td>0.11</td>
<td>0.37</td>
<td>0.48</td>
<td>0.64</td>
<td>1.54</td>
<td>0.61</td>
<td>1.22</td>
<td></td>
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</tr>
<tr>
<td>% change Jnr CB 6.5 mm</td>
<td>64 C</td>
<td>0.04</td>
<td>0.09</td>
<td>0.09</td>
<td>0.20</td>
<td>0.46</td>
<td>0.16</td>
<td>0.38</td>
<td>0.10</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>% R 0.1 PP 1 mm</td>
<td>64 C</td>
<td>0.7</td>
<td>25.8</td>
<td>76.3</td>
<td>46.9</td>
<td>70.4</td>
<td>43.7</td>
<td></td>
<td></td>
<td></td>
<td>80.4</td>
</tr>
<tr>
<td>% R 0.1 PP 2 mm</td>
<td>64 C</td>
<td>0.6</td>
<td>26.0</td>
<td>76.9</td>
<td>42.5</td>
<td>69.5</td>
<td>41.1</td>
<td>65.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% R 0.1 CB 6.5 mm</td>
<td>64 C</td>
<td>2.7</td>
<td>32.0</td>
<td>66.1</td>
<td>45.8</td>
<td>69.1</td>
<td>42.5</td>
<td>66.8</td>
<td>39.4</td>
<td>61.5</td>
<td>83.6</td>
</tr>
<tr>
<td>% R 3.2 PP 1 mm</td>
<td>64 C</td>
<td>-0.4</td>
<td>7.2</td>
<td>68.1</td>
<td>16.7</td>
<td>33.2</td>
<td>15.3</td>
<td></td>
<td></td>
<td></td>
<td>78.2</td>
</tr>
<tr>
<td>% R 3.2 PP 2 mm</td>
<td>64 C</td>
<td>-1.2</td>
<td>6.9</td>
<td>67.1</td>
<td>16.0</td>
<td>34.3</td>
<td>15.4</td>
<td>32.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% R 3.2 CB 6.5 mm</td>
<td>64 C</td>
<td>1.5</td>
<td>27.2</td>
<td>63.6</td>
<td>36.9</td>
<td>56.9</td>
<td>35.1</td>
<td>56.0</td>
<td>34.1</td>
<td>52.9</td>
<td>83.4</td>
</tr>
</tbody>
</table>
In CC geometries, if there is a large difference in the ratio of the inner cylinder to the outer cylinder, greater than 0.9 for constant rate testing or rotation viscosity, there will be a difference in shear rate from the inner to the outer wall (Steffe 1996, Shramm 1994). In the case of creep and recovery testing this may not be a problem because of the short duration of the applied stress and because no constant flow is needed to determine binder properties. To determine the origin of results differences, actual creep and recovery curves generated with the different geometries were evaluated. If the creep portion of the curves differed, then the shear rate may be a problem. For Newtonian binder this is not an issue, and there should be no difference in the shear rate from the inner to the outer walls. This was verified in that the 1-mm gap PP and 6.5 mm gap CB geometries provided the same compliance results. A close look at the actual creep and recovery curves also verified that for the Newtonian PG 64-22 both geometries provided the same results, Figure 7.6.
All three configurations (1-mm and 2-mm gap PP and 6.5-mm gap CB) had the same peak strain in the creep portion of the curve, which indicates that each had the same shear rate. If the shear rate were a problem, then the peak strains for the GTR modified binders should differ. In each case with the GTR modified binders, the peak strains at the end of the creep cycle were the same for all three geometries. The differences in the compliance results were evident in the recovery portion of the tests. This difference is shown for the 10% 30-mesh GTR modified binder, Figure 7.7. In each case, the creep portions of the creep and recovery curves matched, but the recovery portion of the curves differed. This indicates the results differences must be coming from the GTR particles that are interacting and causing higher amounts of recovery for the CB geometries.
The Newtonian PG 64-22 and the highly polymer-modified PG 64-34 provided the same creep and recovery results for all three geometries. These binders are considered to be homogeneous materials even though the styrene–butadiene–styrene-modified PG 64-34 is a two-phase system consisting of a polymer network in the liquid asphalt. The GTR modified binder has discrete particles that interact to increase the viscosity of the binder. In the PP geometry it is only the very outside edge of the plate that sees the higher strains and the largest amount of particle-to-particle interaction. In this case, only a small portion of the rubber particles are mobilized to interact. In the CB geometry, the stress–strain relationship is developed between the inner and outer cylinder.
with a larger gap. Here, many more rubber particles are mobilized to interact, and this interaction is over the full bob height. This increase in particle interaction may be the cause of the results difference from the geometries.

Both PP and CB geometries demonstrated that GTR size and concentration affect the final binder properties. Addition of 10% GTR increased PG 64-22 from a PG 64 to a PG 70 in the PG system and from a 64S to a 64H or 64V in the MP19 specification, depending on which geometry was used. An additional 5% GTR to 15% total GTR again increased the grade one step in each of the systems.

The effect of GTR particle size was also demonstrated by the test results. Here the change from 30- to 20-mesh GTR reduced the improvement in binder grade. The larger 20-mesh GTR did not have as great a stiffening effect on the binder as a similar concentration of the 30-mesh material. In this case 15% 20-mesh GTR had the same stiffening effect as 10% of the smaller 30-mesh GTR. This verifies results from previous studies; however, in this case the larger GTR materials can now be tested (Abdelrahman et al. 1999, Loh et al. 2000, Baumgardner and Anderson 2008).

7.5 Comparative Testing of GTR Modified Binders

For comparison purposes, CB geometry testing, as reported by Baumgardner and D’Angelo (2012), in accordance with the new AASHTO M332 MSCR specification, was also conducted on the GTR binders in subsequent work in Baumgardner et al. (2016). The GTR modified binders yielded identical PG grades in CB testing as reported from AASHTO M320 and AASHTO M332 2-mm gap PP testing. Figure 7.8 presents a comparison of non-recovered creep compliance (Jnr) data from testing via PP and CB.
Figure 7.8

Comparison of Jnr Data from Parallel Plate and Cup and Bob Testing

Figure 7.9 presents a correlation of Jnr data from PP and CB testing of the binders presented in Figure 7.8. Good correlation exists with the exception of some of the binders containing 20 Mesh GTR. PP testing of the 20 mesh GTR modified binders reveals more confounded results specifically at the 10% GTR loading. While it may appear there is less confounding at the 20% GTR loading, this is believed to be a result of particle interaction from the larger 20 mesh GTR in both PP and CB testing. These results are consistent with the findings of Baumgardner and D’Angelo (2012) and support the recommendation of CB testing for binders with larger GTR particles. From Figures 7.8 and 7.9, it is apparent that PP testing at a 2-mm gap is adequate for the 30 mesh and finer GTR particles.
7.6 Summary of GTR Modified Binder Specification Findings

Historically, viscosity increase of the GTR modified binder was measured with rudimental vane viscometers to quantify binder performance characteristics. The Superpave system introduced more accurate tools in the asphalt binder testing system to measure performance characteristics. Testing geometry limitations have meant that Superpave binder tests, specifically high-temperature testing, have generally not been applicable in testing GTR modified binders. This inability to fully test the material has limited the use and adoption of GTR modified binders.

Well-known geometries in the rheology field, specifically coaxial cylinder geometries or CB, can handle the larger particle sizes typically used in GTR. However, these geometries are not familiar in the asphalt industry. The ability of the CB geometry to test neat, polymer-modified, and GTR modified binders was investigated.
Initial evaluations indicated that the CB geometry can provide similar results for the Superpave binder parameter $G^*/\sin \delta$ for the neat, polymer-modified, and GTR modified binders. Test results from the CB were within the single-operator allowable variability of the PP geometry for neat and polymer-modified binders. Variability in results for the GTR modified binder was higher; however, this may be the result of the variability of the binder rather than the testing geometry.

The CB geometry provided similar results for the MSCR test for both neat and polymer-modified binders, but it did not provide similar MSCR test results for GTR modified binder. This difference is believed to be related to differences in GTR particle interaction in the different geometries, because the actual difference in results was in the recovery portion of the test, not the creep portion. Which geometry is more representative of the actual performance characteristics of the binder is still to be determined. This determination was accomplished through testing mixtures prepared from the different GTR modified binders that are reported in the next chapter.

Testing with CB geometries verified the effect of GTR particle size and concentration on the base binder stiffening effect. The CB allows this testing to be conducted on materials with a much larger mesh particle size than could be accomplished with 2 mm gap PP testing.

The initial indication is that the CB geometry can replace the Superpave 1 mm gap PP geometry to test GTR modified binders and provide PG grading of those binders. The CB can also be used to perform MSCR testing on GTR modified binders. Differences in MSCR results may be related to differences in particle interaction between geometries; however, this does not preclude the geometry from being used. Currently
there are no data indicating that the PP geometry represents the real performance characteristics of GTR modified binders.
CHAPTER 8

MIXTURE PERFORMANCE

8.1 Overview of Mixture Performance

Key findings of this chapter have been published in the Journal of the Association of Asphalt Paving Technologists (Baumgardner et al. 2012), presented at the 87th annual meeting of the AAPT, and other work has been submitted for publication consideration (Baumgardner et al. 2016). Each of these documents have a different overall objective relating to this dissertation. Thus, the mixture testing results presented in this chapter are separated into two elements according to their corresponding objective.

The first element presents a comparative observation of dry added GTR plus TOR (GTR Dry) in construction of dense graded asphalt (DGA), open graded friction course (OGFC) and stone matrix asphalt (SMA) mixtures, prepared with granite aggregates, with these same mixtures produced with wet blended GTR plus TOR (GTR Wet) modified binder and standard PG 76-22 SBS modified binder.

The second element presents follow up performance verification testing of binders tested according to recommendations of Chapter 7. While the CB geometry discussed in Chapter 7 provided similar results in MSCR testing for both neat and polymer-modified binders, it did not provide similar MSCR test results for GTR modified binder. This
difference is believed to be related to differences in GTR particle interaction in the
different geometries, because the actual difference in results was in the recovery portion
and not the creep portion of the test. Which geometry is more representative of the actual
performance characteristics of the binder was still to be determined at the end of Chapter
7. This determination is accomplished in this chapter through testing of DGA mixtures
prepared from limestone aggregates and the different GTR modified binders presented in
Chapter 7.

8.2 Background of the Current GTR Dry Addition Concept

Growth of GTR modified asphalt pavements can be credited to successful
production and use of asphalt rubber (wet process) and rubber modified asphalt (terminal
blend) binders in high performance asphalt mixtures. Though dry addition of GTR has
had only limited success in the past, recent efforts have been employed to recycle GTR
by dry addition of rubber in the hot-mix asphalt mixing process using additives and
processing aids such as trans-polyoctenamer (TOR), commercially known as
Vestenamer™ (Hines, 2007). These additives are represented to provide an improved
modified asphalt paving binder by incorporating a small amount of additive into GTR
modified asphalt binder, which in turn leads to easier mixing, reduced tackiness, reduced
cracking, less permanent deformation, lower life-cycle cost, and longer service life
(Burns, 1999). In the dry addition GTR, these processing aids are believed to provide
improved interaction between the asphalt binder and GTR due to observations that
mixtures appear to have the ability to be mixed and compacted at reduced temperatures as
compared to conventional mixtures containing GTR modified binders or GTR dry added
to the mixture. Similar methods exist where TOR is substituted by other processing/compaction aids such as Fischer-Tropsch waxes, ethylene bis-stearamide commercially known as Sasobit™, and Licomont BST™. TOR, as well as these synthetic wax additives, seems to provide observed improvements similar to commercial warm mix additives such as improved coating and compaction (Reinke et al., 2011). Acceptance of these improvements may lead some to ignore the benefits, or lack thereof, of GTR as a binder modifier due to inadequate incorporation of GTR into the binder.

It is known that some “dry add” processes used in the past were unsuccessful and exhibited deleterious results, therefore, of concern is that the possibility exists of constructing poorly performing asphalt pavements compared to more established processes such as asphalt rubber (AR), terminal blended rubber modified asphalt (RMA) and asphalt pavements constructed with asphalt binder modified with synthetic polymers (Epps, 1994; CalTrans, 2005).

8.3 Objectives of Mixture Performance Testing

As discussed, mixture performance testing in this chapter had two major objectives. The first was to conduct laboratory mixture comparison tests to determine whether dense graded hot-mix asphalt (DGA), open graded friction course (OGFC), and stone matrix asphalt (SMA) mixtures can be produced with GTR/TOR modifiers added both to the mix dry and wet blended into the asphalt to meet standard specification requirements (granite aggregates were used). The second objective was to assess performance of DGA mixtures prepared with select binders, of different grades, prepared and tested as discussed in Chapter 7 (limestone aggregates were used).
8.4 Materials Tested in Mixture Performance Evaluations

8.4.1 Asphalt Binders used in Mixture Performance Evaluations

Twelve asphalt binders were tested according to two groups to address the specific objectives. All were based on asphalt cements from Conoco/Phillips Wood River, IL (CPW), either PG 67-22 or PG 64-22, as presented in Chapter 3.

Group I binders, utilized in conjunction with granite aggregates for mixture comparison work in the different mixture types discussed in section 8.2, and moisture sensitivity testing in DGA, consisted of Chapter 3 binders 36 thru 39:

37. CPW origin PG 67-22 modified with pre-blended SBS polymer (proprietary blend) to produce PG 76-22 binder (referred to as PG 76-22 hereafter).
38. CPW origin PG 67-22 with dry added GTR/TOR (referred to as GTR Dry hereafter).
39. CPW origin PG 67-22 with wet pre-blended GTR/TOR modified binder that was lab produced to represent terminal blend crumb rubber and has formulation shown in Table 8.1 (referred to as GTR Wet hereafter).

Table 8.1

<table>
<thead>
<tr>
<th>Material</th>
<th>Product</th>
<th>Weight %</th>
<th>Specific Gravity</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Asphalt</td>
<td>PG 67-22</td>
<td>89.55</td>
<td>1.02</td>
<td>88.88</td>
</tr>
<tr>
<td>Additive</td>
<td>TOR</td>
<td>0.45</td>
<td>0.98</td>
<td>0.47</td>
</tr>
<tr>
<td>GTR</td>
<td>GTR</td>
<td>10.00</td>
<td>0.95</td>
<td>10.66</td>
</tr>
</tbody>
</table>
Group II binders, utilized in conjunction with limestone aggregates for verification of performance of GTR modified binder properties in DGA mixture performance, consisted of Chapter 3 binders 40 to 47, plus an additional hybrid binder, binder 48 also discussed in Chapter 3:

40. CPW origin PG 64-22 modified with sufficient 20 minus GTR to produce a PG 76-22 binder (referred to as 20 Mesh hereafter).

41. CPW origin PG 64-22 modified with sufficient 30 minus GTR to produce a PG 76-22 binder (referred to as 30 Mesh hereafter).

42. CPW origin PG 64-22 modified with sufficient 80 minus GTR to produce a PG 76-22 binder (referred to as 80 Mesh hereafter).

43. CPW origin PG 64-22 modified with 5% 30 minus GTR (referred to as 5% GTR hereafter).

44. CPW origin PG 64-22 modified with 10% 30 minus GTR (referred to as 10% GTR hereafter). This binder was also tested as a PG 76-22.

45. CPW origin PG 64-22 modified with 15% 30 minus GTR (referred to as 15% GTR hereafter).

46. CPW origin PG 64-22 modified with 20% 30 minus GTR (referred to as 20% GTR hereafter).

47. CPW origin PG 67-22 with SBS polymer and GTR (proprietary blend) to produce a PG 76-22 binder (referred to as Hybrid hereafter).

Binder 37, CPW origin PG 67-22 modified with pre-blended SBS polymer (proprietary blend) to produce PG 76-22 binder (referred to as PG 76-22) was also used in the Group II binder study.
8.4.2 Aggregates used in Preparation of Mixtures

Granite aggregates for comparative mixture testing and moisture sensitivity analysis specimens were tested from Rinker Material meeting the requirements as established by the Georgia Department of Transportation (GADOT) (GADOT, 2009).

Limestone aggregates for mixture performance analysis specimens were tested from Mathy Construction meeting the requirements as established by the Wisconsin Department of Transportation (WIDOT) (WIDOT, 2009).

8.5 Experimental Plan for Mixture Testing

As with the work reported by Baumgardner and Anderson (2008), for the Group I binders, GTR was added at a rate of 10% by weight of asphalt binder and was modified with 4.5% TOR based on weight of the GTR loading as described by Baumgardner and Anderson (2008). Though work presented in Baumgardner and Anderson (2008) revealed some binders may require greater than 10% GTR by weight of asphalt binder to achieve a PG grading of PG 76-22, 10% GTR by weight of asphalt binder was selected for this study to represent loadings currently specified by some agencies in commercially available GTR processes implied to provide performance equivalent to PG 76-22 modified binders.

It is understood that a higher loading of GTR would serve to improve PG grade performance. An additional objective was to determine the effect of the specified 10% GTR addition by dry mixing versus wet blending of GTR at the 10% loading as compared to commercially available PG 76-22 formulated to meet the PG 76-22 specification requirements. GTR/TOR wet and dry modified mixture was compared with
dense graded, OGFC and SMA mixtures using styrene-butadiene-styrene (SBS) polymer modifier. Typical dense graded and SMA mixtures often contain some (e.g., 15 to 20%) reclaimed asphalt pavement (RAP), however, in this study each mix type was produced with 100% virgin aggregate. The OGFC mixture contained 0.4% cellulose fibers as per mixture design requirements (GADOT, 2009).

The Group II binders did not contain TOR and were blended according to formulations described for each in Chapter 7 and Section 8.4.1.

8.5.1 Testing of Asphalt Binders used in Mixture Evaluations

At the onset of this work, a noted issue with the Superpave specifications was that the high temperature specification parameter in Table 1 of AASHTO M 320 ($G^*/\sin\delta$) was shown to relate poorly to rutting for many “premium grade,” modified asphalt binders. This led to the development of the multiple stress creep recovery (MSCR) (AASHTO TP 70) test as the replacement for the conventional $G^*/\sin$ parameter. From the MSCR test, the new high temperature specification parameter is determined by dividing the non-recoverable (or permanent) shear strain by the applied shear stress. The result is referred to as non-recoverable creep compliance ($J_{nr}$). In addition, the percent recovery (% recovery MSCR) is also computed which provides a more efficient method of characterizing binder than the current practice elastic recovery (AASHTO T 301).

Group I binder Superpave true grades were determined in accordance with AASHTO M 320 Table 1 with additional MSCR testing and will be discussed further in section 8.6.1.2.
More recently, toward the end of this work, the MSCR procedure has been adopted into a new specification, AASHTO M332. Group II binder SuperPave grading was determined in accordance with both AASHTO M320 Table 1 and AASHTO M332 (MSCR), general PG grade results of this testing is presented in Table 8.2 and will not be discussed further. It should be noted that all GTR binder testing was performed using a 2 mm gap while PG 76-22 and Hybrid binders were tested with the standard 1 mm gap.

Table 8.2

<table>
<thead>
<tr>
<th>Binder</th>
<th>AASHTO M320</th>
<th>AASHTO M332</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grade</td>
<td>Grade</td>
</tr>
<tr>
<td>44. 5% GTR</td>
<td>PG 70-22</td>
<td>PG 64H-22</td>
</tr>
<tr>
<td>45. 10% GTR</td>
<td>PG 76-22</td>
<td>PG 64V-22</td>
</tr>
<tr>
<td>46. 15% GTR</td>
<td>PG 76-22</td>
<td>PG 70E-22</td>
</tr>
<tr>
<td>47. 20% GTR</td>
<td>PG 82-22</td>
<td>PG 70E-22</td>
</tr>
<tr>
<td>37. PG 76-22</td>
<td>PG 82-22</td>
<td>PG 70E-22</td>
</tr>
<tr>
<td>48. Hybrid</td>
<td>PG 76-22</td>
<td>PG 64E-22</td>
</tr>
</tbody>
</table>

For comparison purposes, cup and bob (CB) geometry testing, as reported by Baumgardner et al. (2012), was conducted on the GTR binders. The GTR modified binders yielded identical PG grades in CB testing as reported from AASHTO M320 and AASHTO M332 parallel plate 2 mm gap testing. These results were reported in Chapter 7.

For most of the asphalt binders tested, corresponding mixture testing was performed as described later in this chapter; an exception is PG 64-22 binder with 20% GTR was only tested in binder comparison.
8.5.2 Asphalt Mixture Testing

Asphalt mixtures were prepared as discussed in Chapter 3. All asphalt mixture tests presented in this section were not performed in both elements, only those applicable to the specific objective in consideration were used depending on the binder and aggregate system being tested.

8.5.2.1 Extractions

For control purposes, mixture extractions were performed in accordance with AASHTO T 164 substituting toluene/ethanol (85/15) for trichloroethylene TCE. The toluene/ethanol blend was substituted to provide improved recovery of the additives from the aggregate surface.

8.5.2.2 Mixture Durability – Cantabro

The Cantabro test is an abrasion test designed for testing the durability of Open Graded Friction Course (OGFC) mixtures. Typically the test is conducted on 115 ± 5 mm tall specimens compacted with 50 gyrations of a Superpave gyratory compactor. For the purpose of this study standard Superpave (150 mm diameter by 115 mm tall) gyratory specimens, of each mix type, compacted to air voids previously stated, were produced using short term aged mixture. This test, which is typically used to measure resistance of compacted OGFC specimens to abrasion, is carried out in the Los Angeles abrasion machine (AASHTO T 96).

Mass of the specimen is determined to the nearest 0.1 g, and is recorded as P1. The test specimen is then placed in the Los Angeles abrasion machine without the charge
of steel spheres. The operating temperature should be 25 ± 5°C. The machine is operated for 300 revolutions at a speed of 30 to 33 rpm. The test specimen is then removed, and its mass is determined to the nearest 0.1 g (P2). The percentage abrasion loss (P) is calculated according to Equation 8.1.

\[ P = \frac{P_1 - P_2}{P_1} \times 100 \]  \hspace{1cm} (8.1)

The abrasion loss for each of the three specimens at the same asphalt content is then averaged. Typical recommended maximum average abrasion loss values for OGFC mixes are 20 to 30%, depending on the aging performed (Mallick et al., 2000).

8.5.2.3 Rut Testing

Two laboratory wheel-tracking devices, the Asphalt Pavement Analyzer (APA) and the Hamburg Wheel Tracking Device (HWTD), were used to determine comparative rutting susceptibility of PG 67-22, PG 76-22, GTR Wet and GTR Dry dense mixtures and PG 76-22, GTR Wet, and GTR Dry SMA mixtures.

The APA tracks a loaded aluminum wheel over a pressurized linear hose placed directly on the specimen. For the purposes of this evaluation Superpave gyratory compacted specimens at 7 ± 0.5% air voids (via AASHTO T 166), were tested with an applied load to the aluminum wheel of 445 N (100 lbf), a hose pressure of 690 kPa (100 psi) and a testing temperature of 64°C (147°F).

The HWTD tracks a 47 mm (1.85 in.) loaded steel wheel applied directly to the specimen which is submerged in water that is maintained at 50°C (122°F). Superpave
gyratory compacted specimens at 7 ± 0.5% air voids (via AASHTO T 166), were tested submersed in water at 50°C (122°F) for 20,000 passes.

8.5.2.4 Repeated Creep

A “repeated creep” (RC) test for hot-mix asphalt (HMA) mixture performance was developed using a constant stress dynamic shear rheometer (Reinke and Glidden, 2004). Based on work to date, failure criteria data may be established that would enable this procedure to be used as a mix design tool. The test is rapid enough that quality control monitoring of HMA mixes being placed in the field can be performed and the results can be available within 24 hours. Using the RC test as a performance evaluation test for asphalt mixtures, data generated on specimens cut from field cores have been shown to correlate well ($R^2 > 0.9$) (Reinke and Glidden, 2004) to the field rutting behavior. The RC test was employed in this study in order to evaluate the impact of the binders studied on the various mixture performance evaluations.

The test is conducted using rectangular mixture bars, which are cut from gyratory compacted specimens. Bar dimensions are nominally 50 mm long, 12 mm wide, and 10 mm thick. Specimens are tested using the solids testing fixture provided by the rheometer manufacturer. Specimen test temperature is maintained by air circulation through a temperature-controlled oven that surrounds the specimen. In the RC test a stress is applied to the specimen for 1 s followed by a 9 s rest period of zero stress during which time the specimen recovers some of the strain developed during the 1 s stress period. Repeated stress and relaxation cycles are applied to the test specimen up to 2,000 complete cycles or until specimen failure occurs. From this creep test procedure, several
types of results have been obtained, including time to 2% strain, time to 5% strain, time to minimum first derivative (tertiary flow or Flow Number (Fn) as defined by Biligiri et al. (2007)), time to Tertiary Flow Failure (TFF) (defined by the peak in the cycles/strain vs. time curve (Reinke and Glidden, 2004)), and slope of data in the steady creep region of the test, Figure 8.1. Low slope values are indicative of mixtures that accumulate strain slowly; as a result better performing mixtures have smaller slope values. Therefore to avoid confusion with other parameters where greater values indicate better performance, values of 1/slope are tracked; thus better performing mixtures have larger values of 1/slope. This approach also has the added benefit that the parameter being tracked has values greater than one.

![Figure 8.1](image)

**Figure 8.1**

Analysis of Parameters from Repeated Creep Data
8.5.2.5 Texas Overlay Testing

The Texas Overlay Tester (TXOT), formerly the TTI (Texas Transportation Institute) Overlay Tester, was used to characterize mixture reflective cracking potential (Zhou and Scullion, 2004). The TXOT is designed to test specimens cut from Superpave gyratory compacted samples, therefore, specimens in this evaluation were prepared on the Superpave gyratory compactor in the same manner as those prepared for the HWTD and the APA.

Specimens are affixed to a dual plate fixture with an opening displacement of from 0 to 2 mm (0 to 0.08 in.) and are cyclically tested at a loading rate of 10 s per each cycle for 10 min. at an isolated temperature selected in the range of 0 to 25°C (32 to 77°F). Loading type is typically a one-phase loading in a cyclic triangular waveform with constant maximum displacement. The reflective cracking life of the asphalt mixture is determined based on recorded loading data. Fracture properties of the asphalt mixture can also be evaluated in the overlay tester. TXOT testing parameters used in this evaluation were a gap of 2 mm (0.08 in.) with 5 mm (0.20 in.) tape, temperature of 25°C (77°F) and rate of 1 cycle/10 s at 0.6 mm (0.025 in.).

8.5.2.6 Bending Beam Rheometer Mixture Beams

A straightforward BBR test to determine low temperature binder properties from asphalt mixtures was developed by Zofka et al. (2005). This mixture BBR test was performed concurrent with binder BBR testing, with BBR stiffness testing being performed on mixture beams. In this test the BBR measures the mid-point deflection of a beam of asphalt mixture subjected to a constant load applied to the mid-point of the
beam. The BBR operates only in the loading mode; recovery measurements are not obtained.

Conditioned test beams are placed in the controlled temperature fluid bath at a temperature (e.g. -12°C or -18°C). Mixture specimens are loaded with a constant load (4950 ±50 mN) for 1000 s. The test load and midpoint deflection of the beam are monitored versus time. The maximum bending stress and strain at the midpoint of the beam are calculated from beam dimensions, span length, and load applied to the beam for loading times of 15, 30, 60, 120, 240, 480, and 960 seconds.

Beam stiffness can be calculated two ways. The first is to use measured parameters at discrete times (e.g., 15 s) and calculate stiffness (often referred to as measured flexural creep stiffness), and the second is to fit a second order polynomial to the logarithm of measured stiffness to test time at the aforementioned test times (often referred to as estimated creep stiffness). Estimated creep stiffness was used herein and is denoted S(t).

8.5.2.7 Dynamic Modulus Testing

Dynamic modulus testing was performed using the Asphalt Mixture Performance Tester (AMPT) and dynamic shear torsion-bar (TB) testing.

The AMPT is a computer controlled hydraulic testing machine that subjects a compacted mixture specimen, in the case of this evaluation cut from a Superpave gyratory compacted sample, to cyclic loading that simulates traffic loading. The AMPT measures mixture deformation to assess performance and is typically used to identify performance characteristics of mixes, quality control, and in design of flexible pavements
An AMPT was used in this study to determine dynamic modulus of the dense graded and SMA granite mixtures and to determine the flow time and flow number of each mixture type. An AMPT was also used in this study to determine the effects of moisture on dynamic modulus of the dense graded granite mixtures prepared with each the Group I binder, and to determine the dynamic modulus of the dense graded limestone mixtures prepared with each Group II binder.

8.5.2.8  Modulus from Repeated Creep

As with the RC text, dynamic shear TB testing is conducted on a DSR using rectangular mixture bars, which are cut from gyratory-compacted specimens. Bar dimensions are nominally 50 mm long, 12 mm wide, and 10 mm thick. Specimens are tested using the solids testing fixture provided by the rheometer manufacturer. Specimen test temperature is maintained by air circulation through a temperature-controlled oven that surrounds the specimen.

Oscillatory TB testing was conducted using a dynamic shear rheometer (DSR) in frequency sweeps from 1 to 10 Hertz (6.28 to 62.8 rad/sec) from 25 to 35°C (77 to 95°F) in 2.5°C (4.5°F) increments.
8.6 Test Results and Discussion from Granite Aggregate Mixture Testing

8.6.1 Binder Test Results

8.6.1.1 Results from Extractions

Tables 8.3, 8.4 and 8.5 present data from extraction of dense graded, OGFC and SMA mixes. Gradations after extraction of the lab produced mixtures matched well with the design gradations. Binder contents from extraction of the dense graded mixtures were all acceptable with the PG 67-22 and GTR Dry being slightly above the 5.1% optimum while the PG 76-22 and GTR Wet were slightly lower than the design optimum. All of the dense mixtures yielded recovered binders within the 4.0 to 5.5% range of the reported design (GADOT, 2009).

<table>
<thead>
<tr>
<th>Sieve</th>
<th>Sieve mm</th>
<th>0.45 Power</th>
<th>PG 67-22</th>
<th>PG 76-22</th>
<th>GTR Dry</th>
<th>GTR Wet</th>
<th>Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4&quot;</td>
<td>19.00</td>
<td>3.672</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1/2&quot;</td>
<td>12.50</td>
<td>3.116</td>
<td>98</td>
<td>96</td>
<td>97</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>3/8&quot;</td>
<td>9.50</td>
<td>2.754</td>
<td>87</td>
<td>80</td>
<td>82</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>No 4</td>
<td>4.75</td>
<td>2.016</td>
<td>59</td>
<td>54</td>
<td>56</td>
<td>56</td>
<td>58</td>
</tr>
<tr>
<td>No 8</td>
<td>2.36</td>
<td>1.472</td>
<td>43</td>
<td>40</td>
<td>41</td>
<td>41</td>
<td>43</td>
</tr>
<tr>
<td>No 16</td>
<td>1.18</td>
<td>1.077</td>
<td>30</td>
<td>28</td>
<td>29</td>
<td>29</td>
<td>31</td>
</tr>
<tr>
<td>No 30</td>
<td>0.60</td>
<td>0.795</td>
<td>22</td>
<td>21</td>
<td>23</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>No 50</td>
<td>0.30</td>
<td>0.582</td>
<td>16</td>
<td>15</td>
<td>15</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>No 100</td>
<td>0.150</td>
<td>0.426</td>
<td>11</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>No 200</td>
<td>0.075</td>
<td>0.312</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

Binder contents from extraction of the OGFC mixtures were all lower than the design optimum of 6.1%, with only the GTR Dry binder content being in the 5.5 to 6.5% range of the reported design (GADOT, 2009) and the PG 67-22, PG 76-22 and GTR Wet
all being lower than the specified range at 5.1%, 5.3% and 5.0% respectively, Table 8.3. Extractions were not from compacted mixtures but from loose mix that was oven aged at the compaction temperature. The cause of the low OGFC asphalt contents relative to the design value is unknown, and this difference should be noted as it affects the way data presented later in the paper should be interpreted. The data still have value, but in some instances the relative asphalt contents can affect interpretation of test data. Possible causes of the low asphalt contents include drain down during oven conditioning, insoluble binder components, and laboratory batching errors.

Table 8.4
Extraction Data for OGFC Granite Mixtures in Reference to Design

<table>
<thead>
<tr>
<th>Sieve</th>
<th>Sieve mm</th>
<th>0.45 Power</th>
<th>PG 67-22</th>
<th>PG 76-22</th>
<th>GTR Dry</th>
<th>GTR Wet</th>
<th>Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4&quot;</td>
<td>19.00</td>
<td>3.672</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1/2&quot;</td>
<td>12.50</td>
<td>3.116</td>
<td>93</td>
<td>90</td>
<td>91</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>3/8&quot;</td>
<td>9.50</td>
<td>2.754</td>
<td>55</td>
<td>53</td>
<td>57</td>
<td>53</td>
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<tr>
<td>No 4</td>
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<td>15</td>
<td>16</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>No 8</td>
<td>2.36</td>
<td>1.472</td>
<td>9</td>
<td>9</td>
<td>11</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>No 16</td>
<td>1.18</td>
<td>1.077</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>No 30</td>
<td>0.60</td>
<td>0.795</td>
<td>6</td>
<td>6</td>
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<td>6</td>
<td>6</td>
</tr>
<tr>
<td>No 50</td>
<td>0.30</td>
<td>0.582</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>No 100</td>
<td>0.150</td>
<td>0.426</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>No 200</td>
<td>0.075</td>
<td>0.312</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Asphalt Content</td>
<td>5.1</td>
<td>5.3</td>
<td>5.8</td>
<td>5.0</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Binder contents from extraction of the SMA mixtures were also lower than the design optimum of 6.3%, with only the GTR Wet binder being less than the 6.0 to 6.5% range of the reported design (Table 8.5) (GADOT, 2009). Most of the difference between GTR Wet and design could be attributed to insoluble components of the GTR.
Table 8.5
Extraction Data for SMA Granite Mixtures in Reference to Design

<table>
<thead>
<tr>
<th>Sieve</th>
<th>Sieve mm</th>
<th>0.45 Power</th>
<th>PG 76-22</th>
<th>GTR Dry</th>
<th>GTR Wet</th>
<th>Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4&quot;</td>
<td>19.00</td>
<td>3.672</td>
<td>99</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1/2&quot;</td>
<td>12.50</td>
<td>3.116</td>
<td>93</td>
<td>93</td>
<td>91</td>
<td>91</td>
</tr>
<tr>
<td>3/8&quot;</td>
<td>9.50</td>
<td>2.754</td>
<td>66</td>
<td>63</td>
<td>64</td>
<td>66</td>
</tr>
<tr>
<td>No 4</td>
<td>4.75</td>
<td>2.016</td>
<td>30</td>
<td>32</td>
<td>31</td>
<td>27</td>
</tr>
<tr>
<td>No 8</td>
<td>2.36</td>
<td>1.472</td>
<td>23</td>
<td>23</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>No 16</td>
<td>1.18</td>
<td>1.077</td>
<td>19</td>
<td>19</td>
<td>18</td>
<td>17</td>
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<tr>
<td>No 30</td>
<td>0.60</td>
<td>0.795</td>
<td>16</td>
<td>16</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>No 50</td>
<td>0.30</td>
<td>0.582</td>
<td>14</td>
<td>14</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>No 100</td>
<td>0.150</td>
<td>0.426</td>
<td>12</td>
<td>12</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>No 200</td>
<td>0.075</td>
<td>0.312</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Asphalt Content</td>
<td>6.0</td>
<td>6.1</td>
<td>5.4</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For any of the mixture types (DGA, OGFC, SMA), a portion of the low binder contents may be due to aggregate absorption of binder fractions. The GTR Wet mixtures, as compared to the PG 76-22 and GTR Dry mixtures, may be attributed to the higher content of modifier required to produce a PG 76-22 with GTR with consideration that GTR contains as much as 70% inert materials that would not be soluble in extraction solvents and would therefore become part of the recovered aggregate fines. The GTR Dry resulted in higher recovered binders for all mixture types and is most likely due to the fact that the GTR Dry was a “dry added” component (i.e., not counted as part of the binder; see Section 4) to a mixture to which the target binder content was added for each mixture type.

8.6.1.2 Superpave Performance Grading (PG)

PG grades can be considered using either Table 1 or Table 2 of AASHTO M 320. ASHTO M 320 Table 3 was rewritten into a stand-alone specification for Multi-Stress...
Creep and Recovery (MSCR) or non-recoverable creep compliance, Jnr in 2010 (AASHTO MP 19). Table 8.6 and Table 8.7 of this dissertation present the Superpave binder test data for the PG 67-22, GTR Wet and PG 76-22 binders. It can be observed from these data that considerable differences exist in the products tested. With respect to original binder (non-aged) in Table 8.6, the GTR Wet binder exhibits higher G* and G*/sinδ results than the PG 76-22 binder; however, the separation and forced ductility ratio (FDR) results for the PG 76-22 binder are much better. Only the PG 76-22 binder meets the maximum 75° phase angle (δ) requirements of some state DOTs for a PG 76-22 (e.g., Georgia DOT).

Table 8.6

Original Binder Test Data (tested at 76°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>G*  (kPa)</th>
<th>δ    (deg)</th>
<th>G*/sinδ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG67-22</td>
<td>1.21</td>
<td>86.8</td>
<td>1.22</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>1.88</td>
<td>79.1</td>
<td>1.92</td>
</tr>
<tr>
<td>PG76-22</td>
<td>1.09</td>
<td>67.3</td>
<td>1.18</td>
</tr>
</tbody>
</table>

With respect to aged binder test results given in Table 8.7, the GTR Wet still shows higher G* and G*/sinδ results as compared to the PG 76-22 binder; however, it should be noted that the GTR Wet binder fails to meet the Superpave minimum m-value (m) of 0.300. The PG 76-22 binder also exhibits lower phase angle (δ) and greater AASHTO T 301 elastic recovery (ER) than the GTR Wet binder.
Table 8.7

Aged Binder Test Data (tested at 76°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>RTFO Residue</th>
<th>PAV Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G* (kPa)</td>
<td>δ (deg)</td>
</tr>
<tr>
<td>PG67-22</td>
<td>2.96</td>
<td>83.2</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>4.20</td>
<td>70.0</td>
</tr>
<tr>
<td>PG76-22</td>
<td>2.40</td>
<td>62.6</td>
</tr>
</tbody>
</table>

Table 8.8 presents binder test data on extracted binders from all three mixture types containing PG 67-22, GTR Dry, GTR Wet and PG 76-22 binders. From Table 8.8 it can be seen that the GTR Wet and PG 76-22 binders show increases in G* and G*/sinδ over the RTFO aged binder data, Table 8.7.

The extracted GTR Dry fails to meet the minimum requirements for RTFO aged binders, Table 8.8. While it is not a requirement that extracted binders meet or exceed the minimums for RTFO aged binder, it is expected that they would meet minimum requirements. This is most likely an indication that GTR Dry, especially the GTR portion, does not have sufficient time for complete incorporation into the hot mix binder in the “dry add” process.

Table 8.8

Extracted Binder test data (tested at 76°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>G* (kPa)</th>
<th>δ (deg)</th>
<th>G*/sinδ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTR Dry</td>
<td>1.57</td>
<td>84.0</td>
<td>1.58</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>6.85</td>
<td>76.5</td>
<td>7.07</td>
</tr>
<tr>
<td>PG76-22</td>
<td>2.88</td>
<td>62.8</td>
<td>3.24</td>
</tr>
</tbody>
</table>
8.6.1.3 Non-Recoverable Creep Compliance, Jnr

Results determined from AASHTO TP 70 Multiple Stress Creep and Recovery (MSCR) evaluation are presented in Table 8.9. MSCR testing is typically performed at pavement service temperatures; therefore, testing for this evaluation was performed at the LTPP Bind recommended 64°C. From Table 8.9, it can be seen that only the PG 76-22 binder meets AASHTO MP 19 specification requirements for PG 64V-22 which is designed for use in pavements with “very heavy” traffic loads. Requirements for a PG 64V are a maximum Jnr of 1.0 at 3.2 kPa shear stress with a minimum 50% recovery for the resulting Jnr value of 0.399 kPa for this testing. The GTR Wet binder meets the Jnr requirement for a PG 64H-22 (“heavy” traffic loads) but fails the % recovery requirements for a Jnr value of 1.072 of this testing.

Table 8.9

<table>
<thead>
<tr>
<th>Binder</th>
<th>0.1 kPa Shear Stress</th>
<th>% Recovery</th>
<th>3.2 kPa Shear Stress</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG67-22</td>
<td>4.973</td>
<td>-2.3</td>
<td>5.363</td>
<td>-3.9</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>0.636</td>
<td>37.1</td>
<td>1.072</td>
<td>9.6</td>
</tr>
<tr>
<td>PG76-22</td>
<td>0.349</td>
<td>78.0</td>
<td>0.399</td>
<td>75.1</td>
</tr>
</tbody>
</table>

Table 8.10 presents MSCR test data for recovered binders from three mixture types. There is a substantial difference in the three mixtures. Extracted binders from the dense mixtures are generally stiffer, which may likely be due to lower binder contents and greater aging of the binder. Extracted binder from dense mixture containing PG 76-22 is very different in that the percent recovery is much higher at 85% compared to both GTR Wet and GTR Dry binders as well as the PG 67-22.
Performance of binders extracted from the OGFC mixtures is somewhat puzzling which may be attributed to lower binder contents discussed previously. One would assume that for the OGFC there would be higher binder contents and less aging, but for the GTR Wet and PG 76-22 this does not seem to be the case. They both have very low Jnr compared to the PG 67-22 and GTR Dry extracted binders. The percent recovery for the OGFC are in line with what would be expected, but the PG 67-22 and the GTR Dry both have low percent recoveries, indicating little delayed elastic response or strain tolerance.

Binders extracted from the SMA mixtures are more in line with what would be expected from a magnitude versus percent recovery standpoint. There are significant differences in the Jnr values and these are in line with the percent recovery values. The SMA extracted binders range from a heavy grade to a very heavy to an extreme grade, however, the percent recovery for the GTR Wet seems low compared to the other SMA extracted binders.
Table 8.10

Non-recovered creep compliance/recovery (extracted binders from each mixture type tested at 64°C)

<table>
<thead>
<tr>
<th>Mixture Type/Binder</th>
<th>0.1 kPa Shear Stress</th>
<th>3.2 kPa Shear Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( J_{nr} ) (kPa)</td>
<td>% Recovery</td>
</tr>
<tr>
<td><strong>Dense Mixture</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PG67-22</td>
<td>0.059</td>
<td>45.4</td>
</tr>
<tr>
<td>GTR Dry</td>
<td>0.030</td>
<td>67.4</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>0.042</td>
<td>62.4</td>
</tr>
<tr>
<td>PG76-22</td>
<td>0.011</td>
<td>85.2</td>
</tr>
<tr>
<td><strong>OGFC Mixture</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PG67-22</td>
<td>0.378</td>
<td>24.6</td>
</tr>
<tr>
<td>GTR Dry</td>
<td>0.373</td>
<td>26.1</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>0.018</td>
<td>70.7</td>
</tr>
<tr>
<td>PG76-22</td>
<td>0.036</td>
<td>81.7</td>
</tr>
<tr>
<td><strong>SMA Mixture</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GTR Dry</td>
<td>1.064</td>
<td>14.3</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>0.559</td>
<td>22.9</td>
</tr>
<tr>
<td>PG76-22</td>
<td>0.128</td>
<td>77.4</td>
</tr>
</tbody>
</table>

Typically SMA mixtures combine higher binder content and lower air voids that reduce aging which, in this case, is reflected in the higher \( J_{nr} \) values overall, but with the same ranking as with the extracted binders from the other mix types. The PG 76-22 appears to be the most rut resistant with a higher delayed elastic response in each case. The GTR Dry acts more similar to the neat PG 67-22 in cases of dense and OGFC mixtures. As for the very low \( J_{nr} \) values, it is suspected that there could be considerable fines remaining in the recovered binder that are causing significant increases in binder stiffness. In comparison, the dense graded mixtures would contain higher fines overall, and the OGFC mixtures would have the lowest as there are generally little to no fines in OGFC mixtures. The SMA does have higher filler content, but the very fine generated dust is less due to the high percentage of hard coarse aggregate.

Results of MSCR testing on binders extracted from all mixtures may indicate that dry addition of GTR does not allow sufficient incorporation of the GTR/TOR modifier.
into the mixture to provide performance equivalent to GTR Wet blended or PG 76-22 binders.

**8.6.2 Mixture Test Results for Granite Aggregate Mixtures**

**8.6.2.1 Mixture Durability**

Cantabro test data for dense graded, OGFC and SMA mixtures produced for this evaluation are presented in Table 8.11. As previously stated, the Cantabro test is an abrasion test originally designed for testing durability of OGFC mixtures. While not typically performed on dense graded or SMA mixtures, Doyle et al. (2010, 2011) have reported encouraging results of Cantabro testing on dense graded mixtures and were able to make conclusions regarding RAP content using the Cantabro test on dense graded mixes. Promising results of Doyle et al. (2010, 2011) for dense graded mixtures led to the use of the Cantabro test on all mixture types in this study.

For the dense graded mixtures, asphalt contents were close enough for direct comparison of test results. In the dense graded mixtures, PG 76-22 performed better than PG 67-22, GTR Dry, and GTR Wet. Thirty replicates of two mixtures (one with and without AASHTO R 30 conditioning) were tested by Doyle et al. (2010) at 4% nominal air voids and the coefficient of variation for Cantabro mass loss was 11 to 16%. If this level of variability existed in the Table 8.11 data, two standard deviations above the mean mass loss of PG 76-22 would be 13.1 to 14.1%, and only PG 67-22 falls within this range; GTR modified binders are above the range, indicating a substantial difference in mass loss and, in turn less, durability.
A second example of the mass loss difference between PG 76-22 and GTR modified binders for the dense graded mixtures is made using data from Doyle et al. (2011) measured on dense graded mixtures with 0 to 50% RAP. (One group of mixes was made with limestone and a second was made with crushed gravel.) The change in mass loss between 0 to 25% RAP was 4.1 to 5.8%, and the change in mass loss between 25 to 50% RAP was 4.2 to 5.1%. GTR modified binders increased mass loss 3.8 to 4.1%, which is less (but not tremendously) than what was observed by adding noticeable amounts of RAP to dense graded specimens.

Interpretation of the Table 8.11 OGFC data should consider the binder content corresponding with the mass loss results. PG 67-22 had essentially the same binder content as GTR Wet, yet GTR Wet had considerably less mass loss. PG 76-22 had intermediate asphalt content and performed best in terms of mass loss. While no quantifiable comparisons are available, GTR Wet’s 29.7% loss at 5.0% asphalt content appears comparable to PG 76-22’s 24.5% loss with 5.3% asphalt content. GTR Dry’s next to highest mass loss of 37.1% with 5.8% asphalt (considerably more than any of the other OGFC mixes) is an indication it performed poorer than GTR Wet or PG 76-22, and may have performed worse than PG 67-22 at the same asphalt content. More testing would be required to compare PG 67-22 and GTR Dry OGFC Cantabro performance. Only PG 76-22 and GTR Wet binders produced OGFC with less than 30% mass loss.

Interpretation of the Table 8.11 SMA data should also consider the binder content corresponding with the mass loss results. PG 76-22 had the lowest mass loss at 4.5% and had comparable asphalt content to GTR Dry which had a higher mass loss at 7.2%. GTR Wet had essentially the same mass loss as GTR Dry (7.4% vs. 7.2%) but had 0.7% less
asphalt. GTR Wet performed at least as well as GTR Dry and would likely perform better at the same asphalt content; more would be required to compare GTR Wet and GTR Dry SMA Cantabro performance.

Table 8.11
Cantabro Abrasion Data for Laboratory Produced Mixtures

<table>
<thead>
<tr>
<th>Binder (Content)</th>
<th>Initial Wt.</th>
<th>Abraded Wt.</th>
<th>Grams Loss</th>
<th>Loss (%)</th>
<th>Avg Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dense Mixture</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PG67-22 (5.2)</td>
<td>4569.6</td>
<td>3918.3</td>
<td>651.3</td>
<td>14.3</td>
<td>13.4</td>
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<tr>
<td></td>
<td>4571.7</td>
<td>3994.7</td>
<td>577.0</td>
<td>12.6</td>
<td></td>
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<tr>
<td>GTR Dry (5.2)</td>
<td>4551.8</td>
<td>3850.8</td>
<td>701.0</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4558.8</td>
<td>3909.6</td>
<td>649.2</td>
<td>14.2</td>
<td>14.8</td>
</tr>
<tr>
<td>GTR Wet (5.0)</td>
<td>4567.4</td>
<td>3967.7</td>
<td>599.7</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4655.1</td>
<td>3931.6</td>
<td>723.5</td>
<td>15.9</td>
<td>14.5</td>
</tr>
<tr>
<td>PG76-22 (5.0)</td>
<td>4574.0</td>
<td>4094.1</td>
<td>479.9</td>
<td>10.5</td>
<td>10.7</td>
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<td></td>
<td>4578.0</td>
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<td>497.0</td>
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<tr>
<td>PG67-22 (5.1)</td>
<td>3928.4</td>
<td>2149.9</td>
<td>1778.5</td>
<td>45.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3921.0</td>
<td>2260.2</td>
<td>1660.8</td>
<td>42.4</td>
<td>43.8</td>
</tr>
<tr>
<td>GTR Dry (5.8)</td>
<td>3899.8</td>
<td>2446.8</td>
<td>1453.0</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3873.4</td>
<td>2439.9</td>
<td>1433.5</td>
<td>37.0</td>
<td>37.1</td>
</tr>
<tr>
<td>GTR Wet (5.0)</td>
<td>3850.1</td>
<td>2550.1</td>
<td>1300.0</td>
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<td></td>
</tr>
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<td></td>
<td>3995.3</td>
<td>2975.1</td>
<td>1020.2</td>
<td>25.5</td>
<td>29.7</td>
</tr>
<tr>
<td>PG76-22 (5.3)</td>
<td>3933.1</td>
<td>2925.1</td>
<td>1008.0</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3931.8</td>
<td>3016.0</td>
<td>915.8</td>
<td>23.3</td>
<td>24.5</td>
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<tr>
<td><strong>SMA Mixture</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GTR Dry (6.1)</td>
<td>4423.1</td>
<td>4119.7</td>
<td>303.4</td>
<td>6.7</td>
<td>7.2</td>
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<tr>
<td></td>
<td>4423.5</td>
<td>4089.1</td>
<td>334.4</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>GTR Wet (5.4)</td>
<td>4429.9</td>
<td>4078.4</td>
<td>351.5</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>4441.5</td>
<td>4136.8</td>
<td>304.7</td>
<td>6.9</td>
<td>7.4</td>
</tr>
<tr>
<td>PG76-22 (6.0)</td>
<td>4416.7</td>
<td>4199.8</td>
<td>216.9</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4419.2</td>
<td>4236.6</td>
<td>182.6</td>
<td>4.1</td>
<td>4.5</td>
</tr>
</tbody>
</table>
8.6.2.2 Rut Testing Results

8.6.2.2.1 Asphalt Pavement Analyzer

Rut depth and rutting rate results from APA testing of DGA and SMA granite aggregate mixtures are presented in Figure 8.2. Rutting performance in all dense mixtures was considered acceptable with the PG 67-22 mixture showing the greatest rut depth of 4.7 mm (0.19 in.) at 8000 cycles and the greatest rutting rate of 0.39 mm per 1,000 cycles. Asphalt contents (Table 8.3) were similar between the mixes so direct comparison was used. There were no meaningful differences in rut depths of GTR Dry, GTR Wet, or PG 76-22 DGA mixtures.

SMA test results were not considerably different than dense graded mixtures in the sense that rut depths were acceptable for all mixes. GTR Dry rutted more than GTR Wet or PG 76-22 and its total rut depth and rutting rate were similar to PG 67-22 dense graded mixture. It should be noted, though, that the asphalt content of GTR Dry was noticeably higher in the SMA mixture (Table 8.5) than it was for GTR Wet or PG 76-22. The higher asphalt content explains GTR Dry rutting 1.9 mm more in the SMA than the dense graded mix, while differences were not as large for GTR Wet or PG 76-22.
8.6.2.2 Hamburg Wheel Tracking Device Testing of DGA and SMA Granite Aggregate Mixtures

HWTD rutting results are presented in Figure 8.3. The PG 67-22 dense mixture rutted the most, while GTR Dry, GTR Wet, and PG 76-22 performed in a similar manner. The asphalt contents of all dense graded mixes were essentially the same. All DGA mixes performed in an acceptable manner.

SMA mixes rutted considerably more in the HWTD relative to DGA mixes than they did in the APA. GTR Dry rutted the most, but as stated when considering APA data, it had a higher asphalt content than the other two SMA mixes. GTR Wet rutted less than
PG 76-22, but the difference was less than 1 mm for the SMA mixes at 20,000 load cycles.

![Hamburg Wheel Tracking Device Results (50°C (122°F) Wet)](image)

Figure 8.3
Hamburg Wheel Tracking Device Results (50°C (122°F) Wet)

### 8.6.2.3 Results of Repeated Creep Testing of Granite Aggregate Mixtures

From RC testing, several types of results were obtained, including time to 2% strain, time to 5% strain, time to minimum first derivative (tertiary flow or Flow Number (Fn) according to Biligiri et al. (2007)), time to Tertiary Flow Failure (TFF) (defined by the peak in the cycles/strain vs. time curve (Reinke and Glidden, 2004)), slope and 1/slope of data in the steady creep region of the test. Table 8.12 summarizes these test parameters obtained from the DSR Creep Test data plots.
Table 8.12
Repeated Creep Data, 34 kPa Stress at 64°C

<table>
<thead>
<tr>
<th>Binder</th>
<th>Dense Mixture</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time to 2%</td>
<td>Time</td>
<td>Flow</td>
<td>Tertiary Flow</td>
<td>1/Slope</td>
</tr>
<tr>
<td></td>
<td>Strain (sec)</td>
<td>5%</td>
<td>Number (Fn)</td>
<td>Failure (TFF)</td>
<td></td>
</tr>
<tr>
<td>PG67-22</td>
<td>70</td>
<td>460</td>
<td>1120</td>
<td>2410</td>
<td>209.5</td>
</tr>
<tr>
<td>GTR Dry</td>
<td>320</td>
<td>1740</td>
<td>4500</td>
<td>6000</td>
<td>933.2</td>
</tr>
<tr>
<td>GTR Wet</td>
<td>590</td>
<td>3090</td>
<td>3670</td>
<td>9900</td>
<td>1579.7</td>
</tr>
<tr>
<td>PG76-22</td>
<td>260</td>
<td>1840</td>
<td>7500</td>
<td>9900</td>
<td>1107.0</td>
</tr>
</tbody>
</table>

SMA Mixture

| GTR Dry     | 45            | 170   | 1040  | 1215   | 84.5   |
| GTR Wet     | 115           | 455   | 2000  | 2710   | 195.3  |
| PG76-22     | 85            | 430   | 6850  | 8225   | 663.6  |

Recall that low slope values are indicative of a mixture that accumulates strain slowly; as a result better performing mixtures have smaller slope values. Therefore, to avoid confusion with other parameters where greater values indicate better performance, values of 1/slope were tracked, which means that better performing mixtures have larger values of that parameter, Table 8.12.

Figure 8.4, a plot of permanent shear strain versus time, depicts repeated creep performance of the dense graded granite mixtures. Bearing in mind that each stress and relaxation cycle covers 10 s, it is a simple matter to convert test time to test cycles. Mixtures prepared with PG 76-22 and GTR Wet performed well in the RC test with the GTR Wet mixture performing slightly better with approximately 1% difference at 6000 s. The GTR Dry mixture exhibits equivalent performance to the PG 76-22 and GTR Wet according to the Fn, time to first derivative of Biligiri et al. (2007). However, RC results in consideration of Reinke and Glidden (2004) exhibit TFF of the GTR Dry that would indicate poorer performance than the PG 67-22 and GTR Wet mixtures.
Figure 8.4
Repeated Creep Cumulative Strain Curves for Dense Granite Mixture

Figure 8.5 represents the repeated creep performance of the granite SMA mixtures. From the reciprocal of the slope data in Table 8.12 and the cumulative strain data plots in Figure 8.5, it is evident that the mixtures prepared with PG 76-22 binder perform the best followed by the GTR Wet and GTR Dry mixtures, respectively. The higher asphalt content of GTR Dry should be noted.
8.6.2.4 Results from Texas Overlay Testing

Figure 8.6 presents results of DGA and SMA mixture testing with the Texas Overlay Test (TXOT). It is apparent from these data that SMA mixtures performed better than the DGA mixtures. Additionally the SMA mixtures containing GTR Wet and GTR Dry binders did not perform as well as the SMA mixture produced with PG 76-22 binder. This correlates well with the E* (dynamic modulus) data presented later which shows the SMA mixture produced with PG 76-22 binder to be more stiff in the intermediate temperature range. For comparison purposes, TXOT specification limits for
two TXDOT mixtures types, SMA and Crack Attenuating Mixtures (CAM), are also presented in Figure 8.6.

![Reflective Cracking Life (No. of Cycles)](image)

**Figure 8.6**

TXOT Data @ 25°C (77°F) 2.0 mm Gap, 10 Second Cycles @ 0.6 mm (0.025 in) Displacement

From the data presented in Figure 8.6 it can be concluded that the SMA mixtures produced with the GTR Wet and GTR Dry binders may be more prone to cracking at intermediate temperatures than mixtures produced with the PG 76-22 binder.
8.6.2.5 Mixture Bending Beam Rheometer (BBR) Data for Granite Aggregate Mixtures

DGA BBR data are presented in Figure 8.7. From initial observation of this BBR data, nothing indicates any of the mixtures would be susceptible to low temperature cracking in a PG-22 climate. PG 67-22 and PG 76-22 mixtures show the contribution of the unmodified binder characteristics to low temperature performance in modified binders as BBR curves for mixtures prepared with both binders have similar stiffnesses at both -12 and -18°C.

BBR test results of DGA mixtures prepared with the GTR Wet and the GTR Dry yielded lower stiffnesses than those of the PG 67-22 base binder. At both test temperatures the GTR Dry mixture was the least stiff followed by GTR Wet, PG 67-22 and PG 76-22. The author has unpublished data, as well as data presented in Chapter 6 of this dissertation, that may indicate GTR modification of some asphalt binders can lead to improved low temperature performance. Opinion is this could be due to the contribution of process oils used in compounding of rubber used in tire production. Therefore, reduced stiffness may indeed be related to an improvement to low temperature performance which can only be verified or refuted with further investigation.
Figure 8.7

DGA Mixture BBR S(t) Data at -12°C [A] and -18°C [B]
SMA mixture BBR data are presented in Figure 8.8. As with the dense mixture BBR data, nothing indicates any of the SMA mixtures would be susceptible to low temperature cracking in a PG-22 climate. Note that SMA mixtures with the PG 67-22 were not prepared or tested.

Differences in test results at both -12 and -18°C between mixtures prepared with the PG 76-22, GTR Wet, and GTR Dry binders are not as large as with the dense mixture data. In fact, the PG 76-22 SMA mixture stiffness was less than both the GTR Dry and GTR Wet mixtures at both temperatures, where it was greater in the dense mixtures. The higher binder contents in the SMA mixtures may be the contributing factor to reduced PG 76-22 SMA mixture stiffness. Though both the GTR Dry and GTR Wet SMA mixtures were stiffer than in the DGA mixture testing, the increase in stiffness is not considered substantial. Opinion remains that the reduced stiffness of GTR SMA mixtures may indeed be related to an improvement in low temperature performance due to the contribution of process oils used in the compounding of rubber used in tire production, which again can only be verified or refuted with further investigation.
Figure 8.8

SMA Mixture BBR S(t) Data at -12°C [A] and -18°C [B]
8.6.2.6 Dynamic Modulus (E*)

8.6.2.6.1 E* Testing of Group I DGA and SMA Mixtures

National Cooperative Highway Research Program (NCHRP) project 9-19 recommended three tests to evaluate permanent deformation of asphalt mixtures: E* using the triaxial dynamic modulus test, flow time (Ft) using the triaxial static creep test, and flow number (Fn) using the triaxial repeated load test. Two of these tests were performed on the AMPT for this evaluation, dynamic modulus and flow number.

Figure 8.9 presents E* master curves from AMPT testing at 4, 20 and 40°C for the dense mixtures prepared with Group I binders. Figure 8.10 presents E* master curves from AMPT testing at 4, 20 and 40°C for the SMA mixtures prepared with Group I binders.
From Figure 8.9, as with mixture BBR results presented in Figure 8.7, DGA mixtures produced with the GTR modifier show a tendency to be less stiff at 4°C (39°F) than the PG 67-22 and PG 76-22 mixtures. Data from DGA mixture testing at 4°C (39°F) show similar trends to mixture BBR data. The data presented for testing at 40°C (104°F) and 10 Hz (typical of traffic loading frequency) indicates that the four dense mixtures perform relatively similar with respect to E* and would most likely perform relatively similarly with respect to rutting. This is also in agreement with data from RC testing, with the exception of tertiary flow exhibited by the GTR Dry mixture. The 40°C (104°F) DGA mixture test data also correlates well with both APA and Hamburg rut test results.
From Figure 8.10, it is observed that the SMA mixtures produced with GTR/TOR modifier show a tendency of greater stiffness than the SMA mixture produced with PG 76-22 binder at all three test temperatures. The data presented from testing at $40^\circ$C ($104^\circ$F) and 10Hz (typical of traffic loading frequency) indicates that the three SMA mixtures perform relatively similarly with respect to $E^*$ and would most likely perform relatively similarly with respect to rutting.

![SMA E* from AMPT Testing at 4°C, 20°C and 40°C](image)

**Figure 8.10**

SMA $E^*$ from AMPT Testing at 4°C, 20°C and 40°C

At the 40°C test temperature, all three mixtures perform similarly. In comparison, as the temperature of AMPT testing is decreased to 20° and 4° the SMA mixtures produced with the PG 76-22 binder do not increase in stiffness as much as the GTR mixtures. Stiffness increases at intermediate and low temperatures due to modification
are not necessarily desirable and can lead to performance issues in some cases. Quantification of these effects would require further study; this investigation was for comparative purposes only.

Figure 8.11 presents AMPT data for Fn from testing at 64°C at 600 kPa and 10 psi confining pressure. As stated, the Fn test is a repeated load test designed to predict rutting potential of asphalt paving mixtures. From Figure 8.11, as with the E* data, the SMA mixture produced with PG 76-22 binder shows better Fn performance than the SMA mixtures produced with GTR Wet or GTR Dry binders.
It should be noted that the 64°C test temperature used for Fn testing may be higher than what is recommended for testing of these mixtures, therefore, the Fn data presented for each of these mixtures may be as much as half of what is typical. Tests for these mixtures are typically recommended to be performed at 50°C (122°F).

Performance of the PG 76-22 in the AMPT flow number test is better than the other mixtures with the GTR Dry mixtures performing worse in both mixture types in comparison to the PG 76-22 and GTR Wet mixtures. In both DGA and SMA mixtures the GTR Dry Fn is slightly less than half that of the GTR Wet mixture and less than one third of the PG 76-22 mixtures.

8.6.2.6.2 E* Moisture Sensitivity Testing of Group I DGA Granite Mixtures

DGA mixtures were prepared with Group I and granite aggregates for moisture sensitivity testing. E* testing was performed at 20°C (68°F) on the AMPT to evaluate moisture effects on the dynamic modulus of asphalt mixtures modified with GTR both wet blended and by dry addition to the mixture. At the conclusion of E* testing, remaining specimens were sliced and tested in indirect tension. Figures 8.12 and 8.13 provide E* and tensile strength test results. A total of 96 specimens were prepared (Chapter 3, Section 3.4) and tested with four binders, two saturation levels (un-saturated, moisture saturated), four freeze-thaw (FT) levels (0, 1, 2, 3), and three specimens per combination. Moisture saturation was to 55-60% to begin E* testing.

At the conclusion of E* testing, one of the three specimens in each combination was sliced to produce two IDT specimens. These specimens were not re-saturated and had the amount of residual moisture present from E* testing. Once saturated, specimens
were conditioned to room temperature and thereafter tested at 50 mm/min. It should be noted when interpreting tensile strength data that the amount of damage within any individual specimen, and the relative damage between specimens, is unknown and could have some effect on results.

In Figures 8.12 and 8.13, each master curve is labeled with the binder type, conditioning, number of FT cycles, and tensile strength. For example, the top curve in the Figure 8.12a legend was PG 67-22 binder that was not moisture saturated, experienced 0 FT cycles, and had a tensile strength of 1644 kPa. For all four E* graphs shown in Figures 8.12 and 8.13, unsaturated with 0 FT cycles could be viewed as the control. Specimens were prepared and tested to assess overall durability in the sense that they are exposed to FT cycles without moisture to determine if any degradation occurs, and thereafter subjected to FT cycles with moisture to determine if any behaviors can be attributed to moisture.

Figure 8.12a (PG 67-22) shows no obvious trends and appears to be random variability as the unsaturated specimen absent FT was the lowest master curve, and the three specimens that had 1 to 3 FT cycles were the highest master curves. Exposing a mixture to FT cycles should not increase E*. The four saturated specimens fall within the unsaturated master curve band and align closely with each other. The average level of saturation in Figure 8.12a was 5%. There is no evidence the PG 67-22 binder was affected by moisture when viewing E* data.

Figure 8.12b (PG 76-22) demonstrated similar results to PG 67-22. There was a fair amount of overlap between unsaturated and saturated specimens with no pattern as a function of FT cycles. The only potentially noteworthy item was all three saturated
master curves that experienced FT cycles had lower E* values than the unsaturated control; it is easily possible that this is nothing more than random variability. The average level of saturation in Figure 8.12b was 5%. There is no evidence the PG 76-22 binder was affected by moisture when viewing E* data.
Figure 8.12

$E^*$ Master Curves from AMPT Testing at 20°C,
A – PG67-22, B – PG76-22
Figure 8.13

E* Master Curves from AMPT Testing at 20°C,
C – GTR Wet, D – GTR Dry
Figure 8.13c (GTR Wet) exhibited E* degradation due to saturation. Interestingly, the average saturation level remaining after E* testing was over twice what was experienced by PG 67-22 and PG 76-22 (11% versus 5%). Unsaturated specimens had a progressive E* increase with increasing FT cycles. Saturated specimens did not experience a pattern with regard to FT cycles, but there was no overlap between unsaturated and saturated specimens (unsaturated specimens had higher E* values in all cases). Figure 8.13c provided some evidence that GTR wet was negatively affected by moisture. It should be noted that GTR is not asphalt cement and that asphalt cement does not always equate to asphalt binder. Removal of asphalt cement (i.e. bitumen), in favor of GTR (a material that can take on moisture and swell), may have resulted in the higher saturation levels and in turn the drop in E* values.

Figure 8.13d (GTR Dry) may have experienced slight E* degradation due to saturation. The average GTR saturation level was over three times that experienced by PG 67-22 and PG 76-22 (16% versus 5%). This is intuitive with GTR introduced in a dry process. All saturated master curves have lower E* values than unsaturated master curves, but there is a slight overlap. The data was all tightly grouped with no other identifiable trends. Figure 8.13d provided modest evidence that GTR Dry was negatively affected by moisture.

Tensile strengths were interpreted from the position that the values were approximate since relative damage was unknown and that overall trends were more important than individual measurements. Two FT cycles seemed to reduce strengths relative to 0 FT cycles more than 1 or 3 FT cycles, which is not intuitive. Data averaged over all 8 cases (4 binders, two saturation levels) showed 2 FT cycles to have 93% of 0
FT cycles, whereas 1 and 3 FT cycles showed 103 and 105%, respectively, of 0 FT cycles. As a result, all strengths from FT cycles were averaged and compared to 0 FT cycles to assess freezing effects with and without saturation.

Specimens with GTR (Figure 8.13) were weaker than those without GTR (Figure 8.12) by around 20% when all data was averaged. There were no obvious tensile strength loss issues as the average tensile strength reduction was result of FT (with or without saturation) was 81 to 118%. There was a fair amount of tensile strength variability (for example, 118% of the tensile strength being measured after FT cycles), but trends agreed with E* data.

8.7 Test Results and Discussion from Limestone Aggregate Mixture Testing

8.7.1 Hamburg Wheel Tracking Device Testing of DGA Limestone Aggregate Mixtures

Minimal HWTD differences were observed which was attributed to the performance offered by the aggregate structure of the granite aggregate mixture design. This particular aggregate structure is known to be very robust, which was why it was selected for mixture comparison discussed in Section 8.6.2.2. To assess the other boundary of aggregate behavior in mixture performance verification, a less robust limestone aggregate system was selected to provide greater potential for deformation to potentially provide more differentiation between mixtures prepared with different binder grades. A WIDOT E1-12.5mm NMAS fine graded DGA mixture incorporating Group II GTR modified binders and limestone aggregates was used to prepare mixtures for subsequent rut testing. Figure 8.14 presents the aggregate gradation for these mixtures.
HWTD rutting results are presented in Figure 8.15. While the PG 64-22 DGA mixture rutted the most as expected, HWTD results for the mixtures with GTR modified binders were quite unexpected with the 5% GTR modified binder mixture performing better that both the 10 and 15% GTR modified binder mixtures. These puzzling results prompted verification testing that supported the original results. The most likely answer was deemed to be volumetric in nature.
The term asphalt cement (AC) as used in this dissertation refers to bituminous material only and does not include any non-bituminous modifiers such as SBS or GTR. The term asphalt binder as used in this dissertation refers to everything contained in the binder system including asphalt cement, SBS, GTR, or other miscellaneous additives. The effective volume of asphalt cement ($V_{AC}$), i.e. the volume of bituminous material not absorbed by aggregates, is believed to be important in this discussion and others that follow. Inadequate $V_{AC}$ is believed to be a key factor in Figure 8.15. Having insufficient effective binder to provide the desired resistance to permanent deformation has also been observed by others (e.g. Chehovits 1989).

A gradation adjustment was made to allow for non-bituminous components of the modified binder (Chehovits 1989, Baumgardner et al. 2014) and to allow for additional
need for adequate effective binder. Essentially 50% of a blend sand component was removed. The equivalent value of material was split between the materials (excluding RAP) and recombined. An additional amount of blend sand was added back to the +No 8 screen. This gradation was fairly close to the original but allowed room in the gradation on the No 8, 16, and 30 screens. Figure 8.16 presents the original aggregate structure in comparison to the adjusted aggregate gradation.

![Figure 8.16](image)

Adjusted E1-12.5 mm Limestone Aggregate Gradation Bands

DGA gradation adjustments with GTR modified asphalt designs is not a novel concept, general practice has been to avoid mixtures on the fine side of the maximum density line. Chehovits (1989) suggests, due to the presence of the rubber particles in the GTR modified asphalt binder, that the aggregate gradation for DGA mixtures should be maintained on the course side of the gradation band. In fact, (Chehovits 1989)
recommends avoidance of gradations that plot between the maximum density line and the upper limit of the gradation band.

HWTD rutting results for the mixtures prepared with the adjusted gradation are presented in Figure 8.17. HWTD performance of all mixtures, including the PG 64-22 dense mixture, improved with the adjusted gradation. With the adjusted gradation, GTR modified binder mixtures exhibited performance trends expected and typical of the binder grades reported. These results are supportive of the stated objectives.

![Figure 8.17](image-url)

Figure 8.17
Hamburg Wheel Tracking Device Results for GTR Binders (Adjusted E1-12.5 mm Limestone Mixtures @ 50°C (122°F) Wet)
Figure 8.18 presents HWTD results for mixtures made with the PG 76-22 and Hybrid binders using the original unadjusted gradation. Indications are that these binder formulations are more adaptable to fine graded DGA with gradations such as the original E1 gradation. The maximum rut depth at 20,000 passes for the Hybrid and PG 76-22 binder mixture were 3.7 mm and 5.2 mm respectively. This is a considerable improvement over the failing results exhibited by the original E1 mixtures made with the non-modified PG 64-22 and the GTR modified binders and demonstrates a clear advantage of hybrid binders made with GTR and SBS.

Figure 8.18

Hamburg Wheel Tracking Device Results for PG76-22 and Hybrid Binders (E1-12.5 mm Limestone Mixtures @ 50°C (122°F) Wet)
8.7.2 Results of Repeated Creep Testing of Limestone Aggregate Mixtures

Table 8.13 summarizes DSR Repeated Creep (RC) test results conducted on the Figure 8.14 E1 limestone aggregates. Recall that larger values of 1/slope indicate better performance. Figure 8.19, a plot of permanent shear strain versus time, depicts repeated creep performance of GTR modified DGA mixtures. Bearing in mind that each stress and relaxation cycle is 10 seconds it is simplistic to convert test time to test cycles.

Table 8.13
Repeated Creep Data, E1 Design Blend, 34 kPa Stress at 64°C

<table>
<thead>
<tr>
<th>Binder</th>
<th>Time to 2% Strain (sec)</th>
<th>Time to 5% Strain (sec)</th>
<th>Flow Number (Fn) (sec)</th>
<th>Tertiary Flow Failure (TFF) (sec)</th>
<th>1/Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% GTR</td>
<td>78</td>
<td>336</td>
<td>266</td>
<td>400</td>
<td>91.5</td>
</tr>
<tr>
<td>5% GTR</td>
<td>108</td>
<td>435</td>
<td>348</td>
<td>562</td>
<td>117.1</td>
</tr>
<tr>
<td>10% GTR</td>
<td>1023</td>
<td>4870</td>
<td>2780</td>
<td>6050</td>
<td>1350.4</td>
</tr>
<tr>
<td>15% GTR</td>
<td>1881</td>
<td>5111</td>
<td>5226</td>
<td>6476</td>
<td>2500.0</td>
</tr>
</tbody>
</table>

Mixtures prepared with 10 and 15% GTR performed similarly well in the RC test with the 15% GTR mixture performing best with respect to the 1/slope criteria in Table 8.13. RC results in consideration of (Reinke et al., 2004) exhibit TFF of the 10 and GTR Dry that would indicate better performance than the 0% GTR and 5% GTR mixtures. These results do not align with HWTD results presented earlier.
Figure 8.19

Repeated Creep Cumulative Strain Curves for DGA E1 Limestone Mixtures with Varying GTR Loadings

Figure 8.20 represents the RC performance of the 20 Mesh, 30 Mesh and 80 Mesh DGA mixtures in comparison to DGA mixtures prepared with the Hybrid formulation and the PG 76-22 in the Figure 8.14 E1 mixture. From the reciprocal of the slope data in Table 8.14 and the cumulative strain data plots in Figure 8.20 it is evident that the mixtures prepared with PG 76-22 binder perform the best followed by the Hybrid and the GTR mixtures, respectively. For the most part the 20 Mesh and 80 Mesh GTR mixtures performed equivalently with the 30 Mesh performing the poorest. Additional testing was performed with the Figure 8.16 modified gradation and 30 Mesh binder, and practically the same result was obtained, so these results were not shown for brevity. Overall, RC testing did not provide the same findings as HWTD with respect to aggregate gradation.
effects, but did, generally speaking, provide supporting evidence for the potential of hybrid GTR and SBS binder systems.

Table 8.14
Repeated Creep Data, E1 Limestone Design Blend, 45 kPa Stress at 64°C

<table>
<thead>
<tr>
<th>Binder</th>
<th>Time to 2% Strain (sec)</th>
<th>Time to 5% Strain (sec)</th>
<th>Flow Number (Fn) (sec)</th>
<th>Tertiary Flow Failure (TFF) (sec)</th>
<th>1/Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 Mesh</td>
<td>453</td>
<td>1737</td>
<td>2833</td>
<td>4457</td>
<td>591</td>
</tr>
<tr>
<td>30 Mesh</td>
<td>80</td>
<td>507</td>
<td>687</td>
<td>1277</td>
<td>188</td>
</tr>
<tr>
<td>80 Mesh</td>
<td>733</td>
<td>2807</td>
<td>2250</td>
<td>3340</td>
<td>778</td>
</tr>
<tr>
<td>Hybrid</td>
<td>797</td>
<td>6157</td>
<td>9834</td>
<td>14554</td>
<td>3056</td>
</tr>
<tr>
<td>PG 76-22</td>
<td>131</td>
<td>714</td>
<td>9024</td>
<td>14057</td>
<td>4500</td>
</tr>
</tbody>
</table>

Figure 8.20
Repeated Creep Cumulative Strain Curves for DGA E1 Limestone Mixtures Comparing Various GTR Particle Sizes, SBS and Hybrid Modified Binders
8.7.3 Mixture Bending Beam Rheometer (BBR) Data for Limestone Aggregate Mixtures

Mixture BBR data from testing at -16°C and -22°C are presented in Figure 8.21. Reasoning for testing at -16°C and -22°C, rather than the -12°C and -18°C of the previous section, is that these are the actual temperatures the mixtures will experience in service. Initial observation of these BBR data does not indicate that the mixtures tested at -16°C would be susceptible to low temperature cracking in a PG-16 climate. Data from mixtures tested at -22°C present greater cause for concern. The mixture made with the unmodified PG 67-22 shows similar results when tested at -16°C as previous DGA mixtures containing PG 67-22 binder tested at -12°C and -18°C). However, BBR data from mixture containing PG 76-22 tested at -22°C exhibits much higher stiffness compared to results from -16°C or previous dense mixture results at -12°C and -18°C. The 5% and 10% GTR modified binders tested at -22°C exhibit similar stiffness, only slightly less stiff at the lower temperature, to similar binders in DGA mixtures tested previously at -18°C. The 15% GTR modified binder mixture exhibits much lower stiffness when tested at -22°C than any mixture beams tested to date.

Typically BBR mixture testing will show the contribution of the unmodified binder characteristics to low temperature performance in modified binders as BBR curves for mixtures prepared with both modified and unmodified binders have similar stiffness at a given test temperature. This does not seem to be the case with the mixtures tested at -22°C in this study. While the 0% GTR mixture exhibits greater than expected stiffness, the 5, 10 and 15% GTR mixtures exhibit lesser than expected stiffness values.

It is doubtful that the increase in stiffness of the 0% GTR mixture is solely attributable to increase in stiffness due to the decrease in temperature, however, testing of
multiple replicates on multiple days yielded similar results, some actually being greater in stiffness. As for the lesser stiffness of the 5, 10 and 15% GTR mixtures, if one considers the stiffness of 0% GTR mixture to be somewhat accurate or even if it were more similar to the 5% GTR mixture, the reduction in stiffness might be attributed to reduced asphalt cement volume ($V_{AC}$) in the mixtures containing higher contents of GTR. Under the premise that low temperature properties of the base asphalt cement are key to low temperature performance of modified binders the binders and thus mixtures with higher GTR content would have less bituminous asphalt cement to coat and adhere the aggregates thereby reducing the stiffness of the mixture. This is another supporting point for a hybrid binder system.
Figure 8.21

DGA Mixture BBR S(t) Data at -16°C [A] and -22°C [B]
8.7.4  E* Testing of Group II DGA E1 Limestone Mixtures

E* testing was performed on the AMPT for evaluation of mixtures prepared with the Group II binders. Figure 8.22 presents E* master curves from AMPT testing at 4, 20 and 37°C for mixtures prepared with the adjusted aggregate gradation and the four binders, with 0, 5, 10, and 15% GTR. There are no obvious trends in Figure 8.22, though 15% GTR does have the lowest modulus at all temperatures and at least for a noticeable amount of the frequencies tested.

It is likely that removal of a substantial V_{AC} has affected the 15% GTR mixture in Figure 8.23. A hybrid binder system with SBS and GTR should be able to help with this issue as V_{AC} can remain higher for the same total binder content and polymer loading. Figure 8.23 addresses this issue by comparing five binders that all grade the same (PG 76-22) in terms of their master curves. The binder labeled PG 76-22 uses 0% GTR, the Hybrid binder uses a modest GTR loading, and 20, 30, and 80 mesh all use all GTR, just of different sizes. The results are clear. At 4°C, PG 76-22 and Hybrid outperform the 20, 30, and 80 Mesh binders by a considerable margin. At 20°C, these same two binders perform the best, but the gap between them and the 20, 30, and 80 Mesh binders has narrowed. At 20°C, the Hybrid also outperformed the PG 76-22 by a modest amount. At 37°C, there is convergence on the overall scale of Figure 8.23, but if one changes the scale it can be seen that the Hybrid binder performs best, followed by PG 76-22. There is a modest difference between these two binders and the 20, 30, and 80 Mesh binders. Figure 8.23 clearly shows the potential value in the Hybrid binder system.
Figure 8.22

E* from AMPT Testing of GTR Modified Binders at 4°C, 20°C and 37°C

Figure 8.23

E* from AMPT Testing of GTR, PG 76-22 and Hybrid Binders at 4°C, 20°C and 37°C

240
8.8 Summary of Findings from Mixture Testing

Addition of ground tire rubber (GTR) to asphalt is an accepted HMA practice in hot-mix asphalt production. Modification of liquid asphalt binders with GTR is well established and can provide high performance pavements which aid in reduction of the number of waste tires disposed of in landfills and elsewhere. Additionally, asphalt rubber and terminally blended GTR modified asphalt has been used worldwide for many years. However, dry addition of GTR to asphalt mixtures has prompted concern as to detrimental effects on long term mixture performance, especially fatigue and low temperature performance.

Four asphalt binders were tested, in granite aggregate mixtures, with three methods of modification, in DGA, OGFC and SMA to comparatively evaluate the effect of dry added GTR/TOR in HMA. Physical testing was performed on mixtures containing GTR Wet and PG 76-22 asphalt binders and mixtures produced with GTR Dry (dry added to asphalt mixture).

Results from this dissertation suggest that GTR Dry mixture may not perform as well as GTR Wet or PG 76-22 mixtures. Indications are that the GTR may not be totally incorporated into the asphalt binder in the dry addition process. Caution is advised to obtain the best GTR modified binder possible by using conventional wet blending methods to modify asphalt binders with GTR.

Visual observations of improved coating and compaction made on field projects using dry addition of GTR/TOR to hot mix asphalt mixtures may be solely due to the compaction aid properties exhibited by the TOR. Similar results may also be achievable by other compaction aid additives whether added dry or wet blended. Though TOR is not
marketed as a compaction aid, TOR is marketed as a processing aid in other industries, and these processing aid properties may allow for better aggregate coating of aggregates and compaction of hot-mix asphalt mixtures. Essentially, TOR or similar additives in GTR modified asphalt mixtures may simply perform in a similar manner to warm mix additives (Reinke et al. 2011).
CHAPTER 9
SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

9.1 Summary

A detailed GTR and binder modification literature review was completed including information related to compounding and production of pneumatic tires, composition of post-consumer and synthetic polymers, binder modification principles, and mixture performance data with GTR that includes timelines of GTR’s history, successful GTR practices, and areas where improvement is needed. Throughout the review, polymers were grouped into two broad classes: pre-consumer (e.g. styrene-butadiene-styrene (SBS)) and post-consumer (e.g. GTR). In summary an abbreviated version is presented.

9.1.1 Tire Rubber Summary

Pneumatic tires are designed to fulfill fundamental functions throughout their useful lives like cushioning, damping, transmitting of torque (driving and braking), dimensional stability, abrasion resistance, efficient rolling resistance, and durability. Therefore, modern tires consist of five primary components to meet functional demands: tread, sidewall, steel belts, body plies, and the bead. Subsequently, tires are manufactured
from a number of materials including natural and synthetic rubber, textiles and steel. Tire rubber is a complex, engineered, vulcanized compound. Depending on specific function and performance of a tire, different rubber formulations are based on different polymers and fillers. Low molecular weight ingredients may also be necessary for various tire components. Rubber compounds for tire production are generally made using chemically stable and reactive/unstable materials. During the tire manufacturing process, reactive materials are generally consumed during curing, so that little if any of these materials are found in the finished product. There are actually hundreds of different tire formulations in existence, most of which are proprietary to individual tire companies as each manufacturer has developed their own compounds for specific uses.

Tire compound diversity makes it difficult to recycle old tires into new tires with only a small percentage of material from old tires being reused in new tire manufacturing. Lacking the ability to recycle old tires into new tires, there are a number of other common repurposing methods to effectively reuse rubber. Repurposing of rubber from old tires may include but is not limited to: sports surfacing, tire derived fuel, and GTR for modification of asphalt binders for use in asphalt pavement construction. For purposes of this dissertation, interest was limited to GTR used to modify asphalt binders.

Though the composition of a whole tire is complex, GTR from reclamation of old tires is somewhat different. With reactive and volatile materials consumed in manufacturing and synthetic fibers and steel removed in the GTR reclamation process, the remaining GTR is generally comprised of natural and synthetic rubber; primarily natural rubber (NR) and styrene-butadiene rubber (SBR) cross-linked with sulfur and reinforced with carbon black. Other additives (e.g. aromatic hydrocarbons, antioxidants)
are added to improve workability and prevent aging. NR and SBR, polymers similar in chemical nature to virgin styrene-butadiene (SB) and SBS copolymers currently used to modify asphalt cement, are the functional polymer compounds providing effective modification of asphalt binders making their nature and content in GTR of primary importance to effectiveness in asphalt modification (methods to analyze tire rubber composition are provided in Baumgardner et al. 2014). It is this polymer that is used as the functional polymer remaining in the GTR, which is referred to as post-consumer polymer.

9.1.2 Scrap Tire Market Summary

Once tires are produced and their service lives are complete, attention turns from the items described in the earlier portions of Section 9.1.1 to use as a post-consumer polymer. In 2003 it was estimated that 290 million scrap tires were generated annually and that there was a market for 80% of them. In 2013, there was a market for around 96% of the scrap tires generated (around 3.8 million tons of scrap tires were being generated annually). The largest scrap tire market in 2013 was tire derived fuel. GTR used in asphalt paving represented around 4.2 million scrap tires, or around 68,000 tons of GTR, which is around 2% of the scrap tire market (Scrap Tire Markets 2014). Improved methods of using GTR to modify asphalt binders could be valuable considering there is a large amount of market share growth potential.
There are two primary methods of incorporating GTR that are generally referred to as the “wet” and “dry” processes. The wet process blends GTR with asphalt and allows a prescribed reaction time prior to mixing the GTR modified binder with aggregate. The dry process adds GTR directly to the hot mixed asphalt (HMA) mixture during production, GTR in this process is also known as belt added modifier (BAM) and is usually added directly to the aggregate prior to introduction the binder. Growth in use of GTR modified asphalt pavements can be credited to successful construction of high performance asphalt pavements primarily using GTR modified asphalt binders produced via two versions of the “wet” process: “asphalt rubber,” (AR) commonly referred to as the “wet process” and “rubber modified asphalt” (RMA) also referred to as “terminal blend.”

Agencies specifying AR modified asphalt pavements tend to follow specifications based on their experiences. The format and extent of the specifications from different agencies may be different from each other, but generally they have common components describing the type of product or process, materials including specification and test methods, construction requirements, methods of measurement and basis for payment. Typical AR specification requirements obtained from various agencies are items such as GTR loading, blending temperature, blending time, viscosity, softening point, cone penetration, and resilience (Hicks 2012). Only minor adjustments may be needed to facilitate Superpave binder testing incorporating GTR particles less than 30 mesh, such as increasing the standard dynamic shear rheometer (DSR) plate-plate testing gap from 1
mm to 2 mm. There is room for improvement to some specification aspects, while others need only to be verified.

9.1.4 GTR Modified Asphalt Binder History and Performance

Research on GTR modified binders over the last 50 years confirms a favorable impact of GTR modification. GTR ranks second among the most common asphalt polymer modifiers, behind SBS copolymers. Modern GTR use in paving began in the early 1960s with a highly elastic modified binder and aggregate topping developed for Phoenix, AZ (McDonald 1975). The work expanded into large surface treatment projects along with other crack relief and open-graded surface courses. Initial growth of AR applications included surface treatments, interlayers, and AR open-graded friction courses (Huffman 1980). During the two decades following, AR materials increased as they proved useful in various pavement maintenance functional applications including asphalt concrete, but by far the greatest utilization during this time frame was maintenance applications.

The late 1980’s and early 1990’s were a time of heightened interest in GTR. New York State Laws were amended in 1987 requiring investigation and report on the technical and financial implications of mandating addition of scrap tire rubber to paving materials used in public works. In response, the New York State DOT (NYDOT) commissioned a study in 1989 (Shook et.al 1989). Also in 1989, GTR interest in HMA was shown by the Florida DOT (FDOT) who initiated a study in response to action by the Florida legislature in passing Senate Bill 1192 on Solid Waste Management (Roberts et.al
During the period from 1989 to 1991, a number of agencies constructed projects to evaluate GTR modified asphalt. In 1990, the Virginia DOT (VADOT) began construction of four test sections of GTR modified asphalt concrete (Maupin 1996). Dense graded, gap graded surface mixes, and a base mix were constructed. In 1991, the Georgia DOT (GADOT) constructed a GTR test section (Brown et al. 1997). Also in 1991, Section §1038(d) of the Intermodal Surface Transportation Efficiency Act (ISTEA) required states to use a minimum amount of crumb rubber from recycled tires in asphalt surfacing placed each year beginning with the 1994 paving season. The Intermodal Surface Transportation Efficiency Act (ISTEA) mandate caused a surge of interest in GTR technology prompting several thorough literature reviews (Witczak 1991, Bass 1992, Heitzman 1992, Buncher 1995).

In 1994, a catalog and software database was developed by the University of Nevada-Reno under the National Cooperative Highway Research Program (NCHRP) (McCarthy 1994). The database began with the bibliography developed as part of NCHRP Synthesis 198 (Epps 1994).

The ISTEA mandate was lifted in 1995, under Section §205(b) of the NHS Designation Act, though a significant number of GTR pavement sections had already been placed and national research was fostered. Many states discontinued use of GTR after the mandate was lifted. However, Agencies such as Florida, Texas, and Rhode Island continued GTR use. In 2005, the State of California Public Resource Code Section §42700-42703 legislated the use of GTR.
During the early to late 1990s studies were conducted by a number of agencies utilizing various GTR modification methods. Similar findings were reported by Alaska (Saboundjian et al. 1997), Arizona (Way 1999, Kaloush et al. 2002), South Carolina (Amirkanian 2001), Louisiana (Huang et al. 2002), California (Shatnawi 2007) and Colorado (Shuler 2011). A common theme was improved binder properties of GTR modified asphalt binders and improved mixture performance.

Improved rutting (i.e. high temperature) performance is a typical reason to modify asphalt binders; low temperature properties are usually driven by the asphalt cement utilized in the asphalt binder system. Studies, however, have shown rutting to be more a function of the mineral aggregate character (angularity and gradation) and the percentage of voids filled with binder, rather than of binder stiffness (Cross et al. 1992, Kandhal et al. 1990). This is a key point relative to some of the data presented in this dissertation. The optimum binder content is generally higher when using AR, which can result in better aging properties due to thicker binder films. Conversely, lower lab mix stability has been reported when using AR versus a conventional AC (e.g. Buncher 1995), contesting the claims that mixtures produced with AR reduce deformation potential by increasing mix stability. Addition of GTR may raise optimum binder content and lower laboratory stability results in DGA regardless of mix design methodology. Increased voids in mineral aggregate (VMA) due to opening of the gradation of dense-graded mixtures containing AR makes room for swelled GTR particles. Rubber particles may swell as much as seven times their original size.
9.2 Conclusions

The primary objective of this dissertation, to demonstrate the importance of proper processing of all types of modified bituminous binders, whether they be virgin or post-consumer polymers, was accomplished through secondary objectives as described below.

Chapter 5, “Thermo-gravimetric Test Results,” addressing the first of four secondary objectives stated in Chapter 1, presented a simple efficient instrumental method for compositional analysis of GTR used in modification of asphalt binders for production of asphalt paving mixtures. Specific conclusions from the TGA work of Chapter 5 are:

- TGA appears to be a reasonable method for quantitative evaluation of a recycled (or repurposed) product that has inherent variability.
- Natural and synthetic rubber used by tire manufacturers are in a relatively narrow range, thus making TGA analysis ideal for the broader understanding of compositional analysis of GTR by modified asphalt formulators.
- TGA analysis of GTR composition is a less involved alternative to chemical analysis via ASTM D297 for GTR specification compliance analysis.
- GTR compositional analysis by TGA can provide a better understanding of the total functional polymer content as well as content of non-polymeric materials which may affect mixture performance.

Chapter 6, “Binder Modification,” addressed the second of four secondary objectives stated in Chapter 1, presenting optimization efforts of GTR modified binder formulations with respect to how GTR loading, GTR particle size, processing
temperature and asphalt cement source affect modified binder properties. Key conclusions from Chapter 6 are:

- A 10% GTR loading in most PG64 grade asphalt cements (this appears to be asphalt source dependent) appears sufficient to yield a PG 76-22 binder. At approximately 30% functional polymer available in GTR, 10% GTR is considered to be equivalent to approximately 3% of a high molecular weight, radial, SBS polymer.

- Addition of TOR in GTR/TOR modification showed minimal increases in modified binder stiffness as compared to GTR alone. TOR did not appear to provide improvement in processing or performance of the GTR/TOR modified binder over GTR alone with respect to storage stability of finished binder.

- The TOR supplier recommended a processing temperature of 160°C (320°F), which is considered to be too low and a range of 380°F (193°C) to 410°F (210°C) is recommended for processing of GTR formulations with two (2) hours processing and 200 rpm low shear paddle agitation. High shear agitation or mixing may shorten the duration of blending.

- Based on results of GTR particle size evaluations a range of 30 (600μm) to 60 mesh (250μm) ground tire rubber may be most suitable for GTR modified asphalt formulations when processed according to the procedures employed.

- Modified asphalt binder formulations with various binders from a number of crude sources revealed that quality asphalt paving binders can be produced by co-modification with TOR and GTR. Observations are that TOR/GTR modified asphalt binders have similar characteristics to conventional polymer modified
asphalt binders and that the effect of binder source and binder chemistry is also similar.

Chapter 7, “GTR Modified Binder Specifications,” addressed the third of four secondary objectives stated in Chapter 1, introducing a new DSR testing geometry for performance testing and grading of GTR modified binders. Results of testing GTR modified binders with a CB geometry in a standard DSR indicated that:

- Initial indications are that the CB geometry can replace the Superpave 1-mm gap PP geometry to test GTR modified binders and provide PG grading for those binders. The CB can also be used to perform MSCR testing on GTR modified binders.

- Differences in results from testing of GTR modified binders with PP vs CB geometry was considered to be due to particle interaction in the GTR modified binder.

- Testing with CB geometries is an acceptable alternative for testing GTR binders containing GTR particles greater than 30 mesh. While 2-mm gap PP testing is sufficient for binders containing GTR particles 30 mesh and smaller, the larger gap of CB geometries allows for testing of binders containing GTR particles larger than 30 mesh.

Chapter 8, “Mixture Performance,” addresses the fourth of four secondary objectives stated in Chapter 1, presenting results of testing of GTR modified binders used in various mixture types. Evaluated were performance results with respect to binder effectiveness, mixture durability, rutting/deformation resistance, fatigue performance,
low temperature cracking and moisture sensitivity. From the results of mixture testing the following conclusions were drawn:

- Depending on asphalt source 10% GTR may not be sufficient to produce a PG 76-22 binder or mixture performance equivalent to that of mixtures produced with PG 76-22 modified binders. Some binders may require more, while others could require less, as was reported in Chapter 6 and by Baumgardner and Anderson (2008). Also, in consideration of Baumgardner and Anderson (2008), GTR particle size may also have an effect on final binder properties.

- Comparative mixture test results presented support findings in Chapter 6 and the recommendations of Baumgardner and Anderson (2008). Comparison of wet blended GTR to dry addition of GTR shows differences in binder properties as well as mixture performance at equal GTR loadings in the same base asphalt.

- Dense graded Cantabro testing showed PG 76-22 to be the superior performing binder and that adding GTR to the mixtures exhibited increases in mass loss rivaling RAP addition. Only PG 76-22 and GTR Wet binders produced OGFC with less than 30% mass loss. PG 76-22 was also the superior performing binder in SMA mixtures. Other trends were observed from Cantabro testing, but binder content differences between mixes limited their definitiveness.

- Both APA and HWTD rut testing yielded similar results with all mixtures performing well. The PG 76-22 and GTR Wet mixtures had the best overall rutting performance of the mixtures tested, but the asphalt content used in the GTR Dry SMA mix was higher than the other mixes and should be noted when interpreting this conclusion.
• Dense graded mixtures exhibited poor cracking performance for all binders tested in the TXOT test. According to results in the TXOT test, SMA mixtures produced by addition of GTR Dry modifier and binder modified with GTR Wet may be more prone to cracking at intermediate temperatures than SMA mixture produced with the PG 76-22 binder.

• Mixture BBR testing did not indicate potential low temperature mixture performance issues. In dense graded mixtures, mixes with GTR tended to be less stiff than PG 67-22 and PG 76-22 mixes at both temperatures. In the SMA mixtures, the PG 76-22 was less stiff than the GTR mixtures at both temperatures, which is considered to be due to increased binder content of SMA mixtures.

9.3 Recommendations

This dissertation is a multi-year effort. The work shows parallel plate testing at a 2 mm gap is adequate for binders with 30 mesh and finer GTR particles, with Cup and Bob testing being more suitable for binders with coarser GTR particles. Enhancements beyond these do not appear to be needed at present so the recommendation in this regard is to implement 2 mm gap and cup and bob testing as described herein.

Three areas were identified where enhancements could be beneficial. First, it was observed that properly incorporated GTR works well, but when too high of a loading is used in, for example, fine graded mixes, problems can result. This observation has also been made in past works by others. Those works, however, have, for the most part, not offered data and a framework for use of hybrid binder systems to alleviate this issue while still allowing sustainable use of GTR. Thus, the first suggested enhancement from
this dissertation is to use hybrid binder systems consisting of, for example, SBS and GTR in a wide variety of mixture types. Hybrid binder systems should alleviate, for example, the potential moisture sensitivity observed in dynamic modulus testing presented in this dissertation and problems with fine gradations. The second potential enhancement would be specifying GTR use in the context of virgin polymer replacement. The following section discusses merits of implementing a hybrid bonder approach based on virgin polymer replacement, and the following paragraph recommends additional testing needs for hybrid binder systems.

This dissertation did not make use of low temperature tested specimens of larger sizes. BBR mixture beams have their advantages, but it would be useful to have low temperature properties of a series of polymer modified binders (e.g. traditionally modified with GTR, SBS, hybrid of GTR and SBS). A test method worthy of consideration is instrumented indirect tensile testing leading to creep compliance, resilient modulus and fracture energy. Complimenting these tests with intermediate temperature simi-circular bend testing, wheel tracking and cantabro testing would be logical (aforementioned tests are examples only). A test program of this nature for DGA that includes moisture effects and aging is recommended to build on the findings in this dissertation.

9.4 Merits of Implementing the Recommended Hybrid Polymer Modified Approach

Regarding sustainable infrastructure, the American Society of Civil Engineers (ASCE) has recently made mention of a triple bottom line: environment, economics, and social well-being. A discussion of the implications of GTR use, especially in hybrid
modification packages, would be incomplete if all these issues were not addressed. Within this discussion it should be understood that in service asphalt concrete performance affects every facet of the triple bottom line. Pavements with longer service lives that require less maintenance are environmentally friendly from the perspective that they require less greenhouse gas generating attention per unit of use. Likewise, pavements with longer service lives that require less maintenance are more economical, and more efficiently serve public needs (e.g. less congestion due to maintenance and construction activities), which increases well-being.

With regard to GTR’s role as a modifier in sustainable pavements, there are several parallels with respect to Reclaimed Asphalt Pavement’s (RAP’s) history and use as an ingredient in asphalt pavements. RAP’s first widespread interest occurred in the early 1970’s, and was driven by factors such as raw material shortages, increased asphalt cement prices, and pavement disposal restrictions. Over the next few years, this interest dissipated as a lack of understanding of RAP’s properties and how to properly utilize these properties to produce asphalt mixtures with adequate performance was lacking (e.g. see FHWA 1979). Few engineering driven limits were placed on early RAP usage.

Fast forward 30 to 35 years and one can see that RAP use is currently accepted as a sustainable paving practice that can produce mixtures with good performance, but there are engineering based limits. Howard et al. (2013) provides a literature review related to RAP that documents several projects where RAP contents in excess of 25% have been successfully used. Most of the projects documented would be less than ten years old as of the date of this dissertation. Successful RAP use at relatively high concentrations (20% or more for discussion purposes) has been made possible by numerous
characterization studies where engineering, chemistry, and other first principles have been utilized to understand how to design mixtures with RAP that perform at acceptable levels. An essential component to successfully meeting the criteria of a triple bottom line is good performance. While performance is essential to success, recycling initiatives (e.g. RAP, GTR, shingles, or other) often focus much more on economics and environmental facets of the triple bottom line in early stages of the process (refer back to Chapter 2 and how early GTR use was often mandate driven as opposed to performance driven). These areas are vital, but as discussed in the next few paragraphs, implementation can delay if performance is not duly regarded.

Economics is a key decision making factor for any industry. For purposes of discussion, the price of 20 to 30 mesh GTR was taken as $380/ton ($0.19/lb) delivered, and SBS was taken as $2,280/ton ($1.14/lb) delivered. Both prices fluctuate with time (SBS price has been over $2/lb during supply shortages such as in 2011, GTR prices are much more stable), but the values used herein are reasonable and are a 6:1 ratio (i.e. SBS is 6 times more expensive than GTR).

Figure 9.1 plots the yearly average price of PG 67-22 (or equivalent) from January of 1980 through July of 2015 based on Mississippi’s Index. For some of the earlier years, the material would have been designated AC-30, so Figure 9.1 as a whole should be interpreted as the base unmodified asphalt cement used in Mississippi. Index values generally come out once per month, so each year is the average of 12 monthly values unless otherwise noted. Two distinct regions can be seen in Figure 9.1: 2005 and before where prices per ton were generally $100 to $200, and 2006 and after where prices were greater than $300. The focus of this investigation is 2006 and after; all material
considered in this time frame is easily within the PG grading time frame in Mississippi and is PG 67-22.

Figure 9.1
Mississippi Index Asphalt Cement Prices over Time

GTR is cheaper per ton than asphalt cement during most of this time frame, which is not the case with SBS and was not the case for GTR before 2006 (See Figure 9.1). There is obviously economic inertia to use GTR as a “by-mass” substitute for asphalt cement (even for a given grade), but it cannot be emphasized enough that improper incorporation of GTR into mixes only for the purposes of reducing price is not the most appropriate way to satisfy the triple bottom line since performance can be negatively affected if too much GTR is incorporated for a given set of conditions.
A healthier perspective toward improving the triple bottom line can be seen by looking at Mississippi Index prices for PG 76-22 binder. With the exception of February and April of 2006, Mississippi Index prices were available for PG 76-22 from January 2006 through July of 2015 (109 months of data). Subtracting the PG 76-22 price from the corresponding PG 67-22 price for each month available resulted in the following data. Based on yearly averages, 20 to 27% of the total PG 76-22 price was polymer modification, with the remaining being the base PG 67-22. PG 76-22 prices ranged from $90 to $216/ton higher than PG 67-22, with an average price increase of $138/ton. A relative frequency histogram was constructed and revealed: 26% of the monthly price differentials were $90 to $120/ton, 65% were $121 to $160/ton, and 9% were $161 to $216/ton.

GTR can be used to close the price gap between PG 67-22 and PG 76-22 ($138/ton used as an example) by replacing virgin polymer (e.g. SBS) with GTR. A small GTR addition (1% for example), allows a corresponding removal of SBS (<1%, taken as 0.4% for discussion purposes), a price per ton reduction for PG 76-22, improved sustainability, and no performance effects if the GTR is properly incorporated into the binder. GTR can continue to be incrementally added (and SBS removed) until the point asphalt binder performance suffers. At this point, price reductions can begin to negatively affect the triple bottom line.

Adjusting the focus of discussion to environmentally driven incorporation of GTR, the focus is usually more on the landfill space created (or equivalent) than on the pavements that are produced. Effectively, the amount of GTR incorporated into the mixture is the primary measure of success, irrespective of how the GTR affects mix
performance. As with purely economic decisions, purely environmental decisions can have negative performance implications, with examples presented as follows that parallel RAP’s use in asphalt mixtures.

When studying the history of RAP characterization and performance, one can see that early on there were three primary hypotheses taken: 1) RAP is an inert black rock; 2) RAP binder is fully re-livened and fully blends with virgin binder; 3) RAP binder is partially re-livened and partially blends with virgin binder. Hypothesis 3 has been shown more reasonable over the past several years. It is understood in present day that there are numerous factors that affect how RAP performs in mixtures including: binder properties (RAP and virgin), temperature and time factors associated with mixing and transport, mixing energy, and additives (e.g. rejuvenators). Every one of these categories of factors apply to GTR. For example, virgin binder properties affect incorporation of GTR, mixing temperature and time affect dispersion of GTR, and so forth. As discussed, this dissertation provides a detailed literature review regarding GTR’s properties, and also presents test data that supports the aforementioned assessments of GTR behavior. Too much RAP or too much GTR can be used if there is not a framework for that quantity of material to be successful in the mixture. Simply placing large quantities of GTR into a mix, but not providing suitable conditions for the GTR to be successful performance wise, is environmentally conscious only when looking back at the landfill, not when looking forward to pavement performance. A lesson can be learned from RAP’s history; RAP and GTR are black, but they are not inert.

This dissertation has provided evidence that the asphalt paving industry would benefit from philosophical changes with respect to binders modified with GTR. Lessons
and experience from RAP’s past can benefit GTR’s future and help to advance GTR to an
efficiently used post-consumer polymer at a faster rate than if the industry did not have
the experiences from RAP to draw from. While obvious, the paving industry (or any
industry) occasionally needs to be reminded that the same approach to similar problems
often leads to the same result. Therefore, if the industry insists to take every step with
GTR that was taken with RAP (even though RAP’s timeline is around 15 years ahead of
GTR’s timeline), proper incorporation of GTR (as a two component post-consumer
polymer system) may be a decade or more away. However, the industry could choose to
fast forward a decade or so and begin to utilize GTR with essentially the same principles
as are often used for RAP in present day.

When RAP is used in modest to high quantities, a limit on the amount of virgin
binder that can be replaced with RAP binder is often specified. In the case of GTR, this
same logic could easily be applied, just to virgin synthetic polymer (e.g. SBS). Limiting
virgin polymer replacement should be able to serve the triple bottom line better than what
is often specified in present day (i.e. GTR is not allowed or a fixed GTR loading is
required irrespective of the base asphalt cement properties). A suggested specification
approach (applied to each base asphalt cement and SBS source individually) is to first
modify the asphalt cement to the desired grade and document the SBS necessary to do so
(3% is used later for discussion). Next, the specifying agency determines the maximum
amount of SBS they are willing to allow to be removed in favor of GTR (50% is used
later for discussion). Thereafter, the asphalt binder supplier uses the SBS and asphalt
cement sources, alongside any GTR they choose, to develop a modified binder with a
hybrid polymer system.
For example, take GTR that per mass percent has 0.4% effective polymer and 0.6% materials that are not effective polymer. Also for example, take a base asphalt cement (PG 67-22) that was modified to a PG 76-22 with 3% SBS. Assuming a 1:1 replacement of GTR effective polymer with SBS (a simplified assumption), 1.5% SBS and somewhere around 4% GTR should be able to modify the PG 67-22 to PG 76-22.

Aside from simplifying assumptions for discussion purposes, 1 to 2% SBS and 3 to 8% GTR are reasonable ranges of dosages that should work well in hybrid polymer modification systems to, for example, modify PG 67-22 asphalt cement to PG 76-22 asphalt binder. At these loadings, there is still sufficient SBS to provide the consistent and desirable behaviors the industry has relied upon for several years, while also getting performance benefits from GTR, reducing binder costs, and being environmentally conscious (i.e. improving the triple bottom line). Also, binder modification in these ranges gives suppliers economic and engineering flexibility to match their polymer modification systems to the crude oil sources they are using at the time. SBS/GTR loadings in this range are going to be useable in almost any type of DGA (coarse or fine graded), SMA, or OGFC mixture a contractor needs to produce as the issues documented in this dissertation and elsewhere aren’t expected at lower total GTR loadings. The maximum amount of SBS replacement should be set with the idea of limiting GTR loadings so that mixture performance is improved and more consistent over time. A hybrid approach with better performance is also likely to increase the approximately 2% share of scrap tire use in asphalt paving.
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