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Guayule plant extracts as binder modifiers in flexible (asphalt) pavement mixtures

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GUAYULE PLANT EXTRACTS AS BINDER MODIFIERS IN FLEXIBLE (ASPHALT) PAVEMENT MIXTURES

by

STEVEN MICHAEL LUSHER

A DISSERTATION

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ABSTRACT

The guayule (pronounced, 'why-YOO-lee') plant is a woody perennial shrub that is native to areas of the southwestern United States and northern Mexico, and is a well-documented source of high-quality natural rubber. The U.S. needs a domestic source of natural rubber to allay concerns about its future availability. Cultivation of guayule in North America has been attempted many times since the late 19th century, and companies, including major tire manufacturers, are again investing in guayule research. However, full-scale commercialization of guayule rubber needs established markets for the two basic by-products of guayule rubber extraction: the plant resins (primarily non-rubber compounds) and the bagasse (fibrous residue).

The research objective was to investigate guayule resin for use as a binder modifier in flexible (asphalt) pavement mixtures (FPMs). The bulk of the work occurred from 2006 through 2014 in collaboration with the USDA Agricultural Research Service and the Yulex Corporation. Yulex produced hypoallergenic guayule latex for healthcare applications using a water-based extraction method. Of the many guayule-based materials investigated, an acetone-extractable, residual resin in the dried latex was shown to be an effective recycling agent for FPMs with high contents of reclaimed binder.

Beginning in 2013, the endeavor transitioned to collaborating with Bridgestone Americas and PanAridus. These companies used solvent-based extraction methods for producing tire-quality guayule rubber, thus generating resins as process by-products. The Bridgestone and PanAridus resins, compositionally different from each other, were subjected to limited laboratory evaluations and show promise as binder modifiers.

ACKNOWLEDGMENTS

I extend my deepest appreciation to family and friends, here and gone, who have supported me over these many years…this is for them, especially Mom and Dad. Major thanks go to my committee members: Dr. Richardson, my advisor and champion, Dr. Stephenson, Dr. Samaranayake, Dr. Maerz, and Dr. Schuman. Their support and superhuman patience have been phenomenal.

My appreciation for direct financial support by the following cannot be overstated: the National Cooperative Highway Research Program – Innovations Deserving Exploratory Analysis (NCHRP-IDEA) program; the National University Transportation Center on the Missouri University of Science & Technology (Missouri S&T) campus; the Missouri Asphalt Pavement Association (MAPA). My thanks also go to the Yulex Corporation, the United States Department of Agriculture – Agricultural Research Service (USDA-ARS), Bridgestone Americas, PanAridus, and the Missouri Department of Transportation (MoDOT) for indirect and/or in-kind support.

Many people have contributed to this work. Although some of their names may not appear here, be assured that I treasure their participation in this once-in-a-lifetime task. Some who offered inspiration and/or technical assistance are as follows: Dr. Inam Jawed (NCHRP-IDEA director); Dr. Katrina Cornish (Ohio State University); Dr. Francis Nakayama, Dr. Colleen McMahan, and Dr. Terry Coffelt (USDA-ARS); Dr. William Schloman (University of Akron); Jim Mitchell (Yulex); Dr. David Dierig, William Niaura, and Bob White (Bridgestone Americas); Mike Fraley and Bruce King (PanAridus). Thank you, one and all.

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1. INTRODUCTION

1.1. BACKGROUND

The objective of this study was to evaluate the viability of using extracts from the guayule plant as binder (asphalt cement) modifiers in flexible pavement mixtures (FPMs). Specifically, the goal was to use guayule extracts as recycling agents (RAs). RAs essentially serve as softeners of the age-hardened binders in reclaimed asphalt pavement (RAP) and reclaimed asphalt shingles (RAS) that are increasingly used in FPMs. Consequently, the demand for sustainable, better performing RAs is ever present because 99% of RAP generated in the U.S. is recycled in FPMs [1].

The guayule (pronounced, 'why-YOO-lee') plant is a woody perennial shrub that is native to the Chihuahuan desert of northcentral Mexico and the adjacent Big Bend area of western Texas, and is a well-documented source of high-quality natural rubber. Figure 1.1 shows fields of cultivated guayule in Arizona (photo courtesy of the Yulex Corporation) and the first guayule rubber tire made in 1928.

The U. S. needs a domestic source of natural rubber. The guayule plant (*Parthenium Argentatum*) has the potential to be that source. Cultivation of guayule in North America has been attempted many times since the late 19th century [2] [3] [4] [5]. Today, major tire manufacturers are, once again, cultivating and processing the guayule plant on a research and development level to obtain the natural rubber required in different types of tires [6] [7] [8]. This renewed push to find another source for natural rubber is due in large part to concerns about its future availability. *Hevea Brasiliensis* (commonly referred to as the “rubber tree”) has been, essentially, the only source of commercial-grade natural rubber and is grown primarily in Southeast Asia [9] [10].


Title:
Photograph of First Tire Made From Guayule (Rubber)
Creator/Contributor:
Unknown
Date:
1928 February
Contributing Institution:
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Figure 1.1. Arizona Guayule Fields and First Tire Made from Guayule Rubber

However, to achieve full-scale commercialization of guayule rubber, markets need to be established for the two basic by-products of guayule rubber extraction: the plant resins (non-rubber compounds) and the bagasse (fibrous residue) [3, p. 61] [11].

The successful use of guayule resins as binder modifiers in FPMs could simultaneously serve two purposes:

1. Broaden the market of renewable, bio-based binder modifiers that offer fewer health risks than some petroleum-based modifiers.
2. Provide a critical step in establishing a North American source of high-quality natural rubber, a long-standing U.S. national security goal.

1.1.1. Genesis of Investigation into the Guayule Plant. The impetus to this research began with the viewing of a History Channel Modern Marvels television program about the history and future of rubber [12]. The guayule plant was featured in this program and interest was piqued due to the increasing use of rubberized asphalt in the paving industry. After making several inquiries into the status of the guayule rubber industry, contact was established in late-summer, 2006, with Dr. Francis Nakayama, a recently-retired research chemist formerly with the United States Department of Agriculture, Agricultural Research Service, U.S. Arid Land Agricultural Research Center (USDA-ARS-USALARC). Dr. Nakayama arranged to provide samples of guayule-based materials that had been produced approximately 20 years earlier. Dr. Nakayama's package contained a large piece of black rubber and a one gallon can labeled "derubberized guayule resin." The resin was a very dark green, almost black, fluid with the consistency of honey at room temperature, and it had a piney, pleasant odor. It seemed the resin could have potential as a RA for age-hardened (oxidized) petroleum-based asphalt binder, thus the resin became the focus of further investigation. Figure 1.2 shows the original can of resin.

Encouraging results from limited testing using the USDA-supplied resin in combination with petroleum-based binder prompted the submittal of a proposal in August, 2007 to the National Cooperative Highway Research Program (NCHRP) - Innovations Deserving Exploratory Analysis (IDEA) program as a Type 1 project. The Transportation Research Board (TRB) currently administers three IDEA programs, but NCHRP Highway IDEA was the particular program of the three to which said proposal was submitted. This program, to be referred to simply as NCHRP-IDEA throughout the remainder of this document, is funded through NCHRP by the American Association of State Highway and Transportation Officials (AASHTO). NCHRP-IDEA Type 1 projects are concept explorations that demonstrate the validity of unproven concepts, whereas Type 2 projects develop and test prototypes of proven concepts.

Figure 1.2. Original Can of De-rubberized Guayule Resin

After the initial review by the NCHRP-IDEA committee, a set of questions submitted by the members of the committee was addressed and the proposal was re-submitted in February, 2008. The re-submitted proposal resulted in a 2-year research contract beginning February 1, 2009 and ending January 30, 2011. Thus, the mission was underway and a growing fondness for the plain-looking desert shrub had taken root.

1.1.2. NCHRP-IDEA Type 1 Project. U.S. liquid asphalt and road oil refinery stocks and net production are decreasing and flat-lined, respectively, and the trends are shown in Figure 1.3 [13] [14].

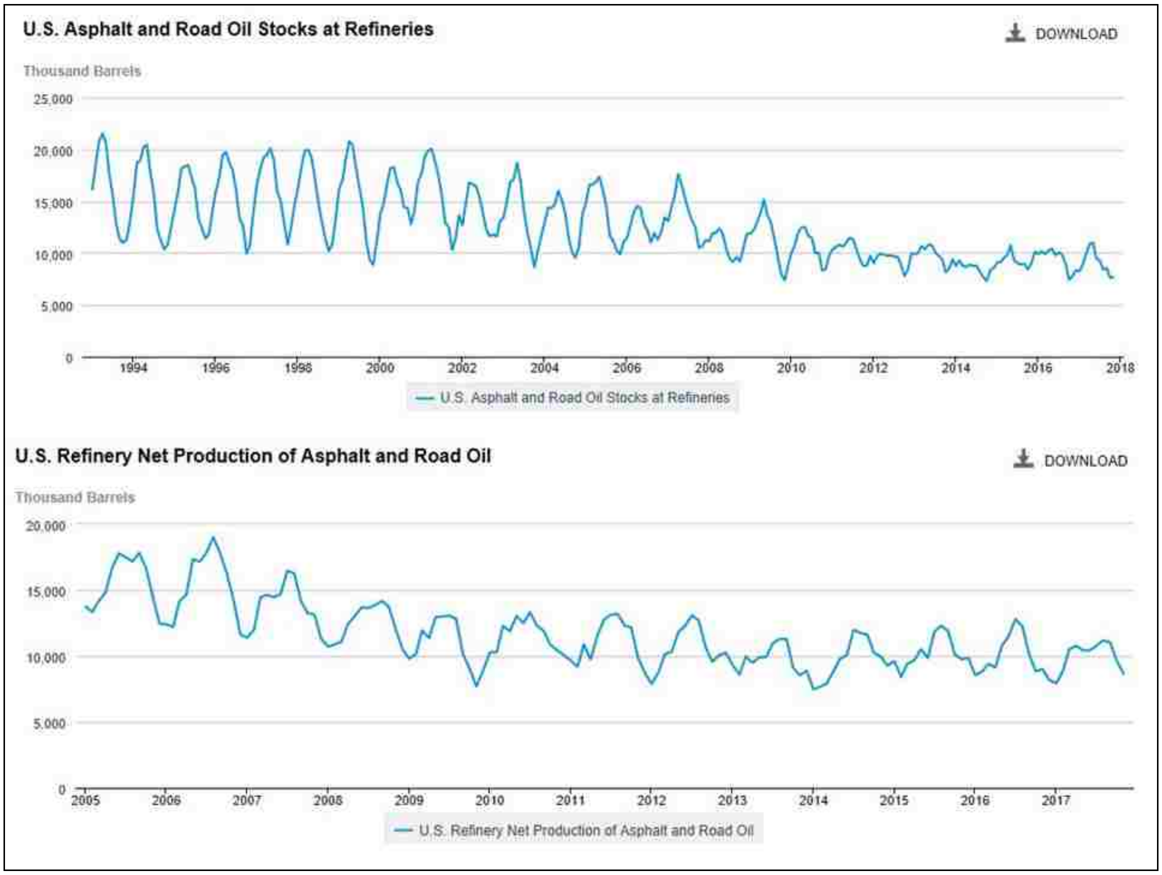


Figure 1.3. U.S. Asphalt and Road Oil Supply Trends

These trends are a result of the combination of increased demand for higher value products like gasoline and diesel fuel, and new refining technologies (e.g. cokers) that make it easier to further refine the heavier, residual oils into those lighter fractions. Additionally, a 2016 survey performed by the National Asphalt Pavement Association concluded, "...The use of recycled materials, primarily reclaimed asphalt pavement (RAP) and reclaimed asphalt shingles (RAS, either processed tear-off roofing shingles or roofing shingle manufacture waste), in asphalt pavements conserves raw materials and reduces overall asphalt mixture costs, as well as reduces the stream of material going into landfills. The combined savings of asphalt binder and aggregate from using RAP and RAS in asphalt mixtures is estimated at more than $2.1 billion" [1].

The factors described above have resulted in the increased use of RAP and RAS, which, consequently, has increased the demand for recycling agents (RAs). RAs have traditionally been petroleum-based binder modifiers that fall into one of two functional classes: softening agents that simply reduce the viscosity of age-hardened RAP/RAS binders, or rejuvenating agents that are intended to return age-hardened RAP/RAS binders to their original state by reducing their viscosity and restoring depleted maltenes (petroleum resins and oils) [15]. However, depending on the refining process and resulting chemical composition, particular petroleum-based RAs (e.g. aromatic or paraffinic oils) may be classified as a carcinogen [16] [17]. This potential health issue and the inevitable depletion of crude oil reservoirs have created the opportunity for bio-based solutions.

There are several bio-based RAs on the market at this time. Some are characterized as rejuvenators, others are not. Two that are regularly used by paving contractors in Missouri are Hydrogreen^{TM}S and Evoflex^{TM}CA. The formulations are proprietary but they are derivatives of tall oil, a by-product of the paper manufacturing process [18] [19].

The NCHRP-IDEA Type 1 project concept was to design, produce, and evaluate a FPM with little-to-no virgin (recently produced) petroleum-based binder. This implied using high percentages of RAP and/or RAS, and a bio-based binder modifier, i.e. guayule resin as a RA. Originally, the proposed research plan was based on using the ~20 year old, USDA-supplied, de-rubberized guayule resin for the entire project. However, it became clear by the end of the fifth quarter (15th month) of the project that further dependence on the USDA-supplied guayule resin as a research material would be unrealistic primarily because, as it turned out, there were only a few gallons of it in existence. Initial concerns about the feasibility of using the USDA-supplied resin began during the fifth quarter of the project as a result of problematic attempts to perform a clay-gel chromatography procedure on the resin to determine whether it was contaminated with mineral oil and/or an antioxidant. Additionally, the process that would have been required for replication of the USDA-supplied resin seemed somewhat of a mystery based on analysis of the pertinent literature [11] [20] [21] and extensive communication with researchers familiar with the history of the resin [22] [23] [24]. Therefore, the decision was made within the fifth quarter of the project to generate research materials by extracting and recovering guayule-based materials from various guayule plant feedstocks (e.g. chipped whole-shrub, waste-stream leaves and stems).

Ultimately, there were two extensions of the project performance period requested and approved. Delays in procurement of key testing equipment during the first year of the project resulted in submission of a request for a nine month, no-cost extension and in January, 2010, an extension of the original research contract was granted, changing the end of the performance period to October 31, 2011. However, the decision to abandon the use of the USDA-supplied resin and generate guayule-based materials in the laboratory was very consequential, caused a significant increase in the scope of the project, and, therefore, required another nine month, no-cost extension request. This request was submitted on August 23, 2011. Dr. Inam Jawed, the NCHRP-IDEA director, approved the extension thereby moving the end of the performance period to July 31, 2012. The draft final report was submitted on July 31, 2012, reviewed, edited, and approved. The final report was submitted for publication on January 16, 2013. Publication by NCHRP-IDEA of the final report occurred in May, 2013 [25]. On December 22, 2014, a paper based on the NCHRP-IDEA report was published online by the American Society of Civil Engineers (ASCE) in its peer-reviewed Journal of Materials in Civil Engineering [26].

Beginning in 2013, the endeavor transitioned to collaborating with Bridgestone Americas (BSA) and PanAridus. These companies used solvent-based extraction methods for producing tire-quality guayule rubber, thus generating resins as process by-products. The BSA and PanAridus resins, compositionally different from each other, were subjected to limited laboratory evaluations. Details of the testing and results are included in this study.

More details on the major collaborators and associated events that helped shape the journey over the last 12 years are given in Appendix A.

1.2. OBJECTIVE

The primary objective of the research was to determine the viability of guayule resins for use as binder modifiers in FPMs. Depending on the extraction process, the resulting resin may be used as a RA to allow for the use of high contents of RAP and/or RAS, and/or the resin can contain some low molecular weight rubber that may improve the elastic and/or high-temperature performance properties of the blended binder.

There was, however, a secondary objective. Although there are several bio-based binder modifiers currently on the market, successful commercialization of guayule resins as domestically-sourced, bio-based binder modifiers would not only add diversity to that market, but could have a significant (and arguably more important) secondary effect: helping to establish a domestic source of natural rubber, a long-standing U.S. national security goal.

2. LITERATURE REVIEW

2.1. THE GUAYULE PLANT

The guayule plant is a woody perennial shrub that is native to the Chihuahuan desert of northcentral Mexico and the adjacent Big Bend area of western Texas. Figure 2.1 shows the areal extent of the native habitat, but it can be grown, and has been grown in other arid or semi-arid regions such as Australia and South Africa [3, p. 10] [27].

First discovered near Escondido Creek, Texas, in 1852 by J. M. Bigelow, M.D., the guayule plant was first described by Professor Asa Gray of Harvard University in 1859 [1, pp. 3-4]. Consequently, one may see the scientific name for guayule stated in the literature as "*Parthenium Argentatum* Gray." However, guayule, along with other rubber-producing plants, had been used for centuries by indigenous peoples of the Americas for making rubber balls for sports and toys by chewing the bark of said plants [1, p. 5] [4, p. 1]. The plant was also used for fuel in Mexican adobe smelters and bread ovens. The high resin content causes the plant to burn with high heat [1, p. 6]. The plant was not popular, however, with the cattle ranchers of colonial Mexico because their cattle would graze on the plant and accumulate rubbery masses in their rumen [5, pp. 23-24].

The first time guayule was brought to the U.S. public's attention was in 1876 as part of a display by the Mexican state of Durango at the Centennial Exposition in Philadelphia, Pennsylvania [1, p. 7] [28, p. 3] [5, p. 24].

In 1888, the first endeavor into extracting guayule rubber for commercial purposes was carried out by the New York Belting and Packing Company after importing 100,000 pounds of shrub from Mexico. The bark was first removed from the shrub, ground up, and then immersed in hot water to remove the rubber [28, p. 3] [29, p. 5].

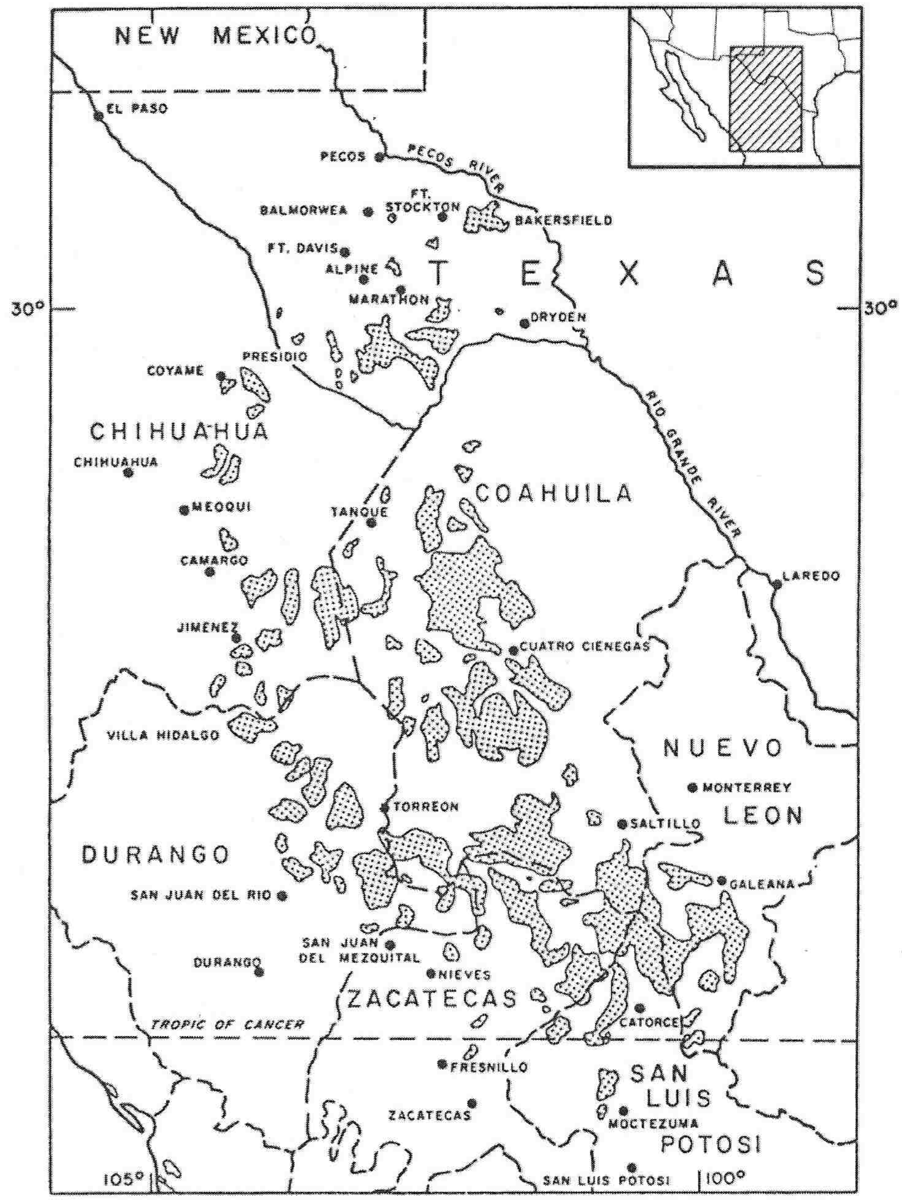


Figure 2.1. Native Habitat of Guayule in North America

The shaded/dotted areas south of the heavy line in Figure 2.2 indicate the locations of approximately 5 million acres in the U.S. that were deemed climatically suitable for guayule cultivation in 1944 [3, pp. 6-7].

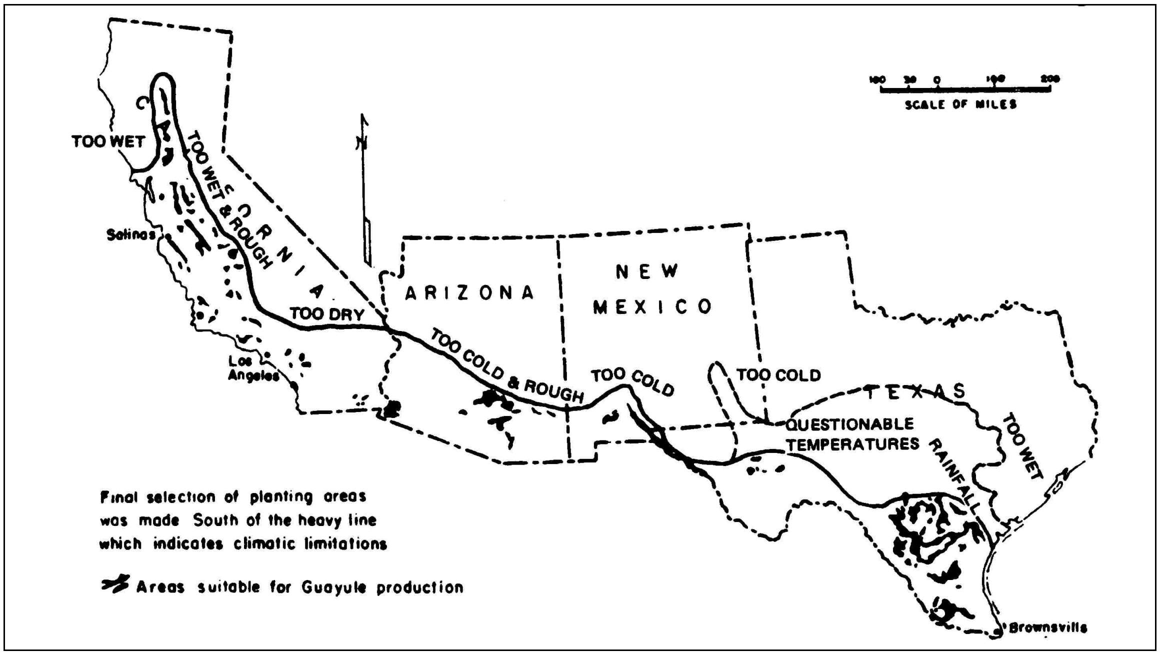


Figure 2.2. Climatically Suitable Areas in the U.S. for Guayule Cultivation in 1944

In 1902, William A. Lawrence began development of the pebble mill, a mechanical extraction process which was implemented successfully in 1904. It remained a primary method for guayule rubber extraction until the end of World War II [29, p. 5]. There were, however, other investigations into guayule exploitation around the turn of the century by the British, Germans, and Italians [1, p. 7] [5, p. 24].

1903 ushered in the organization of the Continental Rubber Company in New York, and in 1904, Continental-Mexican Rubber Company was incorporated and built a small mill in Torreón, Coahuila, Mexico [29, p. 5].

In 1909, the first American guayule rubber processing mill was established in Marathon, Texas, by the Texas Rubber Company. Unfortunately, it had a short debut of about 9 months before shutting down, re-opening in 1925, and then shutting down again in 1926 before eventually being dismantled [28, p. 3].

Between 1900 and 1907, more than twenty guayule processing companies were operating in Mexico [5, p. 24]. 1910 was a high mark when approximately 21 million pounds of guayule rubber were produced. This quantity represented between 10% and 50% of U.S. rubber importation/usage, depending on the reference cited [5, p. 23] [4, p. 13] [3, p. 1].

When the Mexican revolution began to break out in 1911, Continental-Mexican Rubber Company mills and plantations in Mexico were targeted by the revolutionaries. As the story is told, William B. McCallum, a botanist working for Continental-Mexican Rubber, smuggled guayule seeds out of Mexico to the U.S. in 1911, beginning the first significant effort to grow guayule in America [5, p. 23]. The first stop for McCallum was near San Diego, California, where research resumed but on a reduced basis. Soon, however, McCallum had the research facilities relocated to an area south of Tucson, Arizona. Eventually, the company, now known as International Rubber Company, moved to Salinas, California in 1925 [4, p. 13] [29, pp. 5-6].

In the years just prior to 1914, the year World War I began, poor management of Mexican guayule plantations and the onset of the Mexican revolution had severely curtailed guayule rubber production. Political, industrial, and military leaders had come to realize by the time WWI started, just how important natural rubber was, and how vulnerable nations were when the great proportion of natural rubber (*Hevea Brasiliensis*) used by the world came from, essentially, one area on the planet; southeast Asia and the adjoining islands (e.g. Malaysia, and Indonesia). Efforts grew with urgency to cultivate and extract natural rubber from plants growing in the U.S., and luminaries like Thomas Edison, Henry Ford, and Harvey Firestone spearheaded some of those efforts [5, p. 2] [5, pp. 74-106].

In the 1920s, guayule exploitation in the U.S. experienced a surge when the British government played the monopoly card by raising prices on Hevea rubber from colonial plantations in Malaysia. But then there was The Great Depression in 1929, which brought the British plan to a halt [3, p. 18].

On June 6, 1930, a report was issued by Major Dwight D. Eisenhower and Major Gilbert Van Wilkes which made the case that it was incumbent on the U.S. to consider guayule cultivation and rubber production. According to the report, 96% of the world's rubber supply came from Southeast Asia. However, no action was taken until early 1942, just months after Pearl Harbor [29, pp. 3-4]. Coincidentally, on December 7, 1941, The New York Times ran an article about guayule and its potentiality as a source of domestic natural rubber. The article was titled, "U.S. Grows Own Latex" [5, p. 140].

Within weeks of Pearl Harbor, the Japanese had seized rubber plantations and the supporting facilities/logistics in Southeast Asia and the western Pacific Ocean. In February, 1942, Singapore fell, and as Eisenhower and others had warned 12 years earlier, the U.S. and the Allies were now cut off from at least 95% of their rubber supply [5, p. 140].

In March of 1942, the U.S. Congress established the Emergency Rubber Project (ERP). The ERP was established just after the U.S. purchased International Rubber Company (IRC), headquartered in Salinas, California. The ERP became a major priority during the war effort. Salinas became a boomtown and the Manzanar War Relocation

Center at Manzanar, California, was utilized as a research facility with interred Japanese Americans providing scientific and nursery expertise [5, pp. 149-157]. Figure 2.3 shows fields of guayule seedlings and harvesting activity in Salinas [30], and Figure 2.4 shows Manzanar internees out in the guayule fields and working with guayule beds in a lath house [30] [31]. There were other War Relocation Centers, like Poston, Arizona, and 17 labor camps that housed families and single men, many of whom were Mexican Nationals and some German prisoners [28, pp. 54-56].

Eventually, the war came to an end and the ERP was shut down in 1946. The existing land leases were cancelled and 30,000 acres of guayule were burned and plowed under, destroying approximately 21 million pounds of rubber [29, p. 7]. Even more incredulous, 230,000 pounds of guayule seed was sold to a Bakersfield farm supply for cattle food [5, p. 219].

With the crisis ended, interest waned, again, and only Mexico continued to develop guayule in a significant way over the next couple of decades [3, p. 22]. However, there were two other major reasons for the decreased post-war interest in guayule rubber: the rapidly developing use of petroleum-based synthetic rubber and the reacquisition of the Southeast Asian Hevea plantations.

But, in 1973 came the oil embargo and another guayule “revival” [5, p. 229]. Cries for a need to invest in renewable resources grew louder and in 1978, Congress passed the Native Latex Commercialization Act [5, p. 231], and in 1979, the Guayule Rubber Society was created but changed its name to the Association For The Advancement of Industrial Crops in 1988 [32].

Figure 2.3. Guayule Seedling Fields (top) and Harvesting (bottom); Salinas, CA

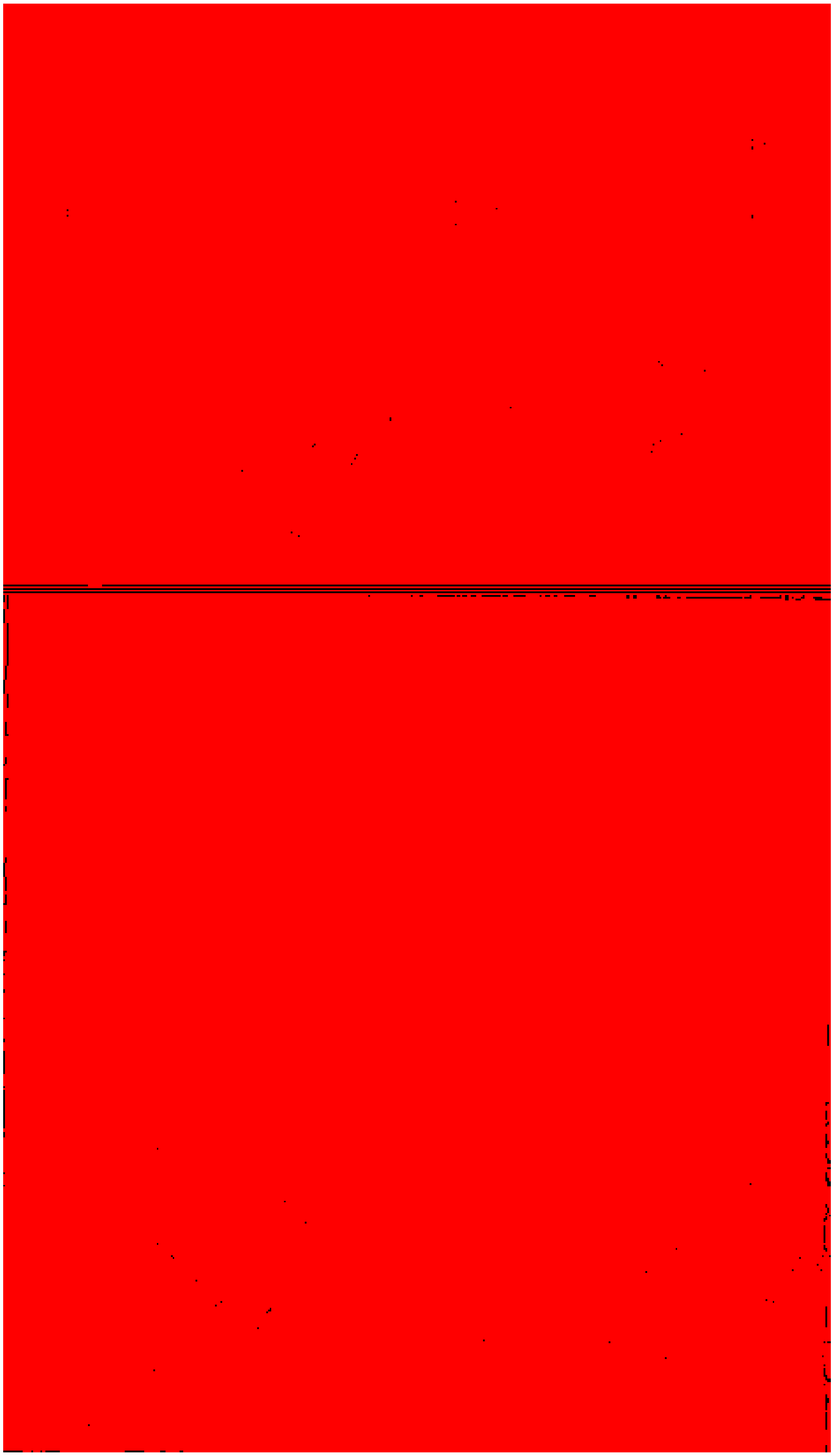


Figure 2.4. Guayule Fields and Guayule Beds in Manzanar War Relocation Center

There were a few more starts and stops in the 1980s and 1990s. During the Reagan administration, there was a fear that the Nicaraguan Sandinistas would cut off overland transit of Brazilian natural rubber which prompted work by Firestone Tire and Rubber (eventually Bridgestone) between 1983 and 1990 to establish a domestic guayule rubber industry. It was during this time that the original de-rubberized resin supplied by Dr. Nakayama to the author was generated at a pilot plant built by Firestone Tire and Rubber in Sacaton, Arizona, in 1987. Then in the early 1990s, the AIDS crisis hit and in response to major health issues created by the large number of allergic reactions to Hevea latex products, research efforts focused on the hypoallergenic properties of guayule rubber [33] [34].

In 1999, Yulex Corporation was founded and marketed hypoallergenic guayule latex for safe medical devices and specialty consumer products. By 2015, Yulex had stopped work with the guayule plant and focused efforts on cleaning up Hevea rubber by removing 99% of the proteins and impurities that contribute to allergic reactions. Their new product is called YulexPure, and it is used to produce a foam that replaced neoprene in wetsuits [35].

As discussed in the Introduction, the most recent activities involving the guayule plant are being undertaken by Bridgestone Americas, PanAridus, and other tire manufacturers and suppliers. These companies are pursuing their commercial interests which has happened in the past regarding efforts at guayule cultivation in the U.S. However, there are also governmental research projects currently being administered by the USDA that involves industry and academia [36] [37]. Thus, it seems that interest in the guayule plant is certainly not waning…at this moment in time.

2.1.1. Rubber. Guayule rubber (GR) is the second-most exploited natural rubber (NR) in world history, with Hevea being number one. Although there are approximately 2500 plant species that produce NR, Hevea and GR top the list as the two most utilized in commercial applications [3, p. 1]. The reason for this ranking can be summarized by two physical properties: molecular weight (MW) and molecular weight distribution (MWD). These properties generally determine the processability of a NR, with higher MW values indicating greater processability [38, p. 6].

Swanson, Buchanan, and Otey [39] evaluated 33 NR producing plants from northern temperate zones, along with Hevea and guayule. They ranked all 35 species according to the MW of the extracted NR and reported that Hevea and GR were the top two ranked species having MW values of 1.310 $(10)^6$ and 1.280 $(10)^6$, respectively, and MWD values of 5.2 and 6.1, respectively. The number three ranked species was mountain mint (*Pycnanthemum incanum*) with a MW and MWD of 0.495 $(10)^6$ and 4.0, respectively. The highly significant gap between the mountain mint NR and GR vividly illustrates the rubber industry interest in GR.

Interestingly, however, another plant species is once again gaining interest in the NR industry: *Taraxacum kok-saghyz*, also known as Russian Dandelion. This plant produces NR with a MW comparable to Hevea [40]. Russian Dandelion was also investigated as part of the Emergency Rubber Project (ERP) during World War II [41].

Unlike the Hevea rubber, which is tapped as latex from ducts within the rubber tree, GR exists in parenchyma cells within the bark and woody tissue. Thus, the shrub must be milled (e.g. chipped, flaked) to rupture the cell walls and release the GR. There are three basic procedures to extract GR and resin: flotation, sequential extraction, and simultaneous extraction. The flotation method is the oldest method of the three. It is a water-based method that has evolved somewhat over time but is the same concept used by Yulex to extract the hypoallergenic latex. The ground shrub is mixed in a dilute alkaline-aqueous solution whereupon resinous rubber “worms” coagulate, float to the surface, are collected through skimming, and are then subjected to further processing. Figure 2.5 shows a flowchart of the water-based process used by Yulex [42].

Deresination of the rubber worms with a polar organic solvent (e.g. acetone) has been traditionally performed before further processing of the GR, but there are several modifications that can be made to this basic procedure to generate different products.

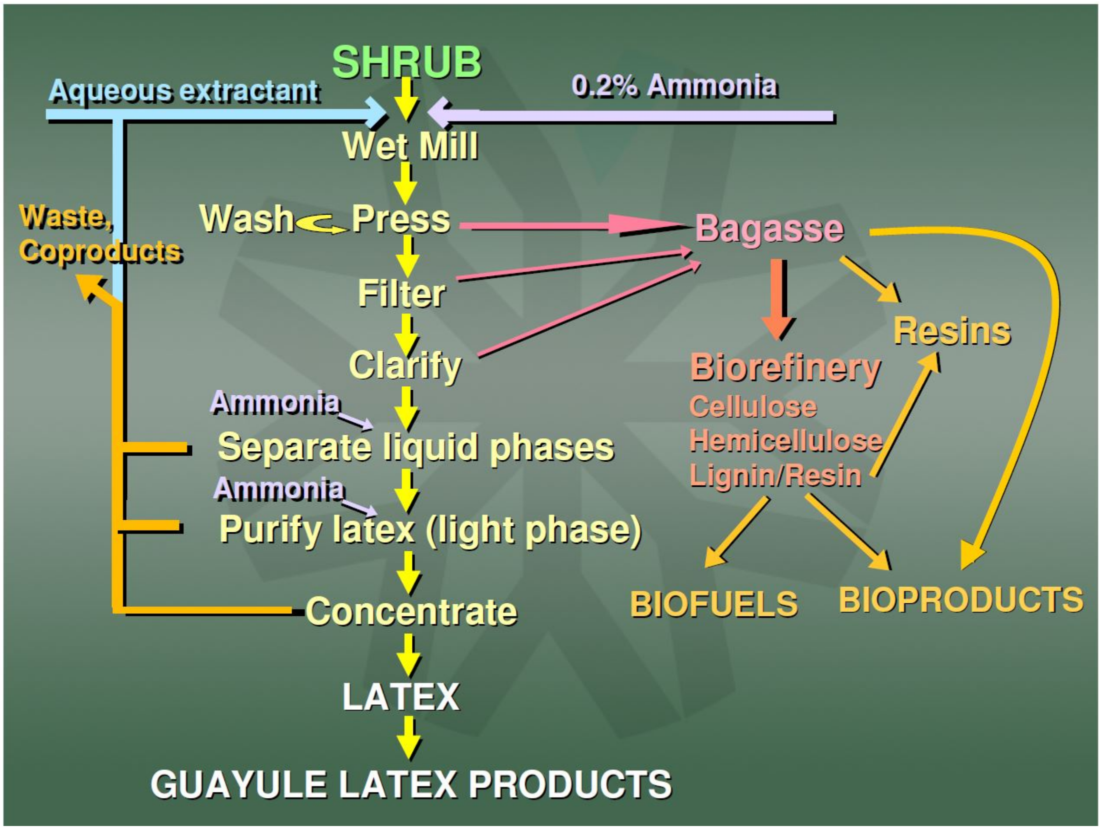


Figure 2.5. Yulex Guayule Latex Extraction Process

The sequential extraction process usually starts by deresinating the ground shrub with acetone before using a polar solvent (e.g. pentane or hexane) to extract the GR. Figure 2.6 shows an example of a sequential extraction process [11, p. 267].

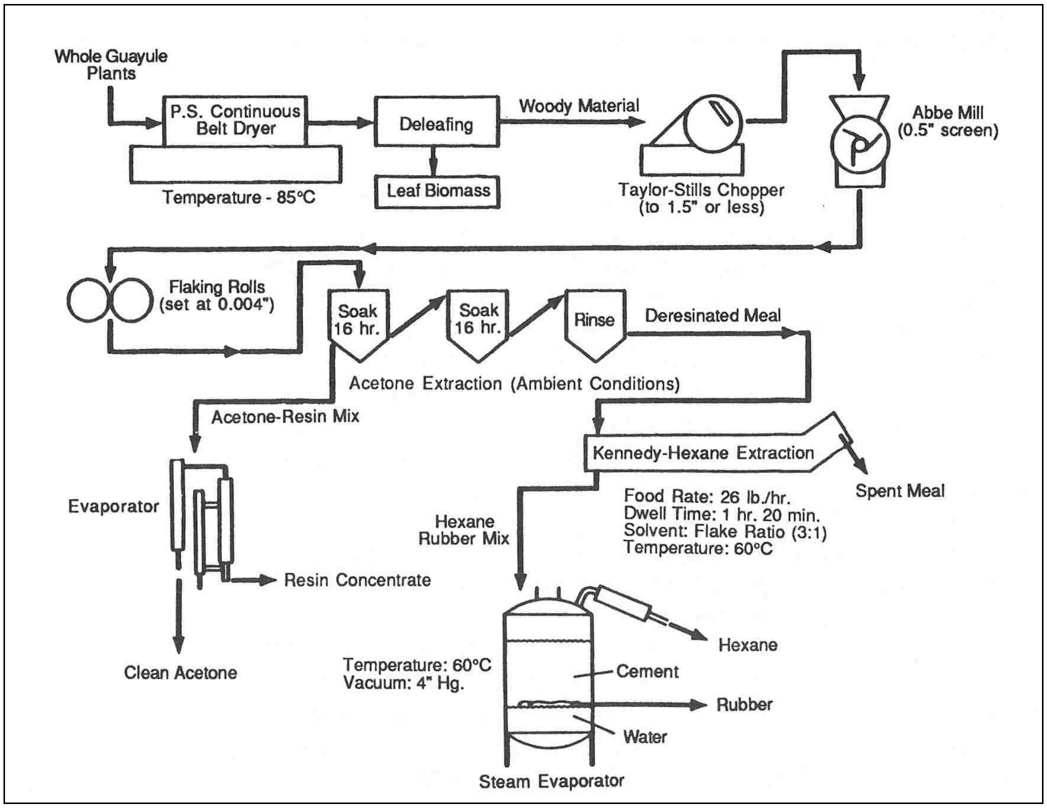


Figure 2.6. Sequential Extraction Process

Yulex experimented with several different processes through the duration of this study. One process was similar to the sequential process described above in that the ground shrub was deresinated with acetone before further processing. In that process, Yulex collected the resin for further evaluation on their part but it was not used for this project. However, a major part of this study did involve samples of dried latex that were supplied by Yulex. The dried latex contained residual resin which was extracted using acetone. Yulex also ran a supercritical fluid extraction experiment and supplied a sample of that material to Missouri S&T. However, there was no action taken with that material.

The simultaneous extraction process is currently being used by Bridgestone Americas and PanAridus. In this process, the GR and the resin are extracted simultaneously by using a mixture of polar (e.g. acetone) and non-polar (e.g. hexane) solvents. The resulting rubber-resin-solvent solution (miscella) is treated with additional polar solvent and the GR coagulates, precipitates out and is collected for desolventization and baling. Figure 2.7 shows the Bridgestone/Firestone simultaneous extraction process [11, p. 279].

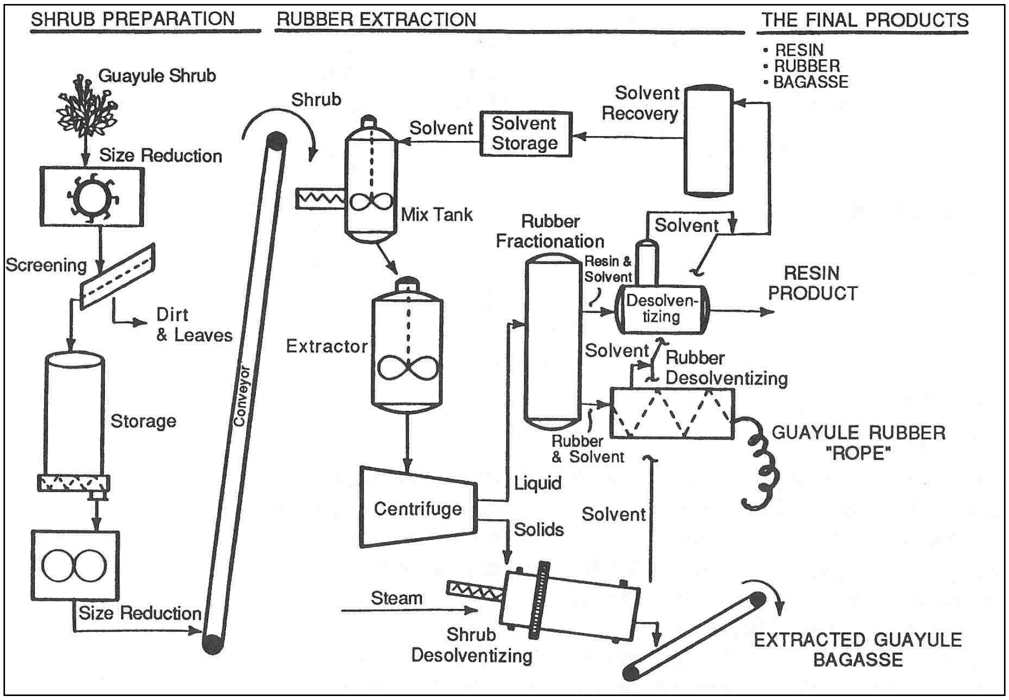


Figure 2.7. Bridgestone/Firestone Simultaneous Extraction Process

The simultaneous extraction has a major advantage over the other methods in that the final physical properties of the GR can be better controlled. Engineering parameters such as the number of fractionation stages and temperature for each stage are key to producing a quality GR for tires and other rubber products.

2.1.2. Bagasse. Guayule bagasse, the fibrous residue leftover after GR extraction, has been, and continues to be the subject of considerable investigative work. Dr. Nakayama, the guayulero first contacted at the beginning of the project, has investigated the use of bagasse to make composite particle board that is termite- and decay-resistant. Depending on the processing history, bagasse can have significant amounts of residual resin and rubber [43], and has been studied as reinforcement in thermoplastic composites [44]. The bagasse has an 8000 to 9000 BTU per pound content and can be pelletized for heating fuel [45]. Pelletizing the bagasse for sale as a fuel was common practice by Yulex during the period of this study. Guayule bagasse has been investigated as a nonfood source of bio-fuel using the fast-pyrolysis process [46]. Ethanol has also been produced using bagasse [45]. The intent is to develop a market for the bagasse by-product to help promote the GR industry.

2.1.3. Resin. Unlike the GR which resides in cells within the bark and woody tissue of the plant, the guayule resin is in ducts that are found throughout the shrub [3, p. 27]. Depending on the extraction process, the chemical makeup of the resin can vary significantly. The resin contains terpene-based compounds, fatty acid triglycerides, and low MW GR. Terpenes have the isoprene molecule, C_5H_8, as the building block. Figure 2.8 shows the isoprene molecule.

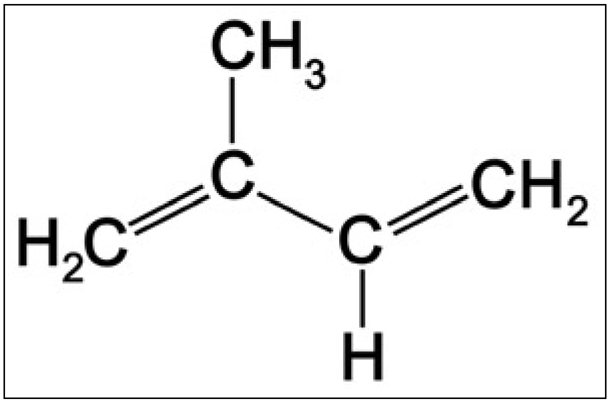


Figure 2.8. Isoprene Molecule (C_5H_8)

Terpenes are mostly single-digit multiples (n) of the isoprene unit $(C_5)_n$ which builds up the carbon skeleton. The monoterpenes (i.e. two isoprene units or $C_{10}H_{16}$) α- and β-Pinene, and Limonene, are very interesting in that they are natural solvents. Pinenes are the basic compounds in turpentine while Limonene is used extensively in "citrus" cleaners. Increasing the number of isoprene units results in sesquiterpene (C_{15}), diterpene (C_{20}), or triterpenes (C_{25}). Terpenoids are isoprene structures with some functional groups attached. Many terpenes are sometimes referred to as essential oils. The major acetone-extractables of the woody tissue are sesquiterpene esters (10-15%), fatty acid triglycerides (7-19%), and triterpenoids (27%) [47].

Guayule resin has been investigated as a termite-resistant coating for wooden construction components [43], a viscosity modifier in natural rubber cement, and an adhesion modifier [48] [49]. The resin could serve as a chemical feedstock for extracting terpenes which can be used for various applications: food, cosmetics, pharmaceutical and biotechnology industries [50]. The low MW GR, a low viscosity, unavoidable product of primary processing, can be used as a plasticizer [49] and has been investigated as a precursor in high solids, ultra-violet cured, and water-borne coating formulations [51]. Powder, marine, and peelable coatings have been formulated using the low MW GR and resin [52]. Currently, Bridgestone Americas is burning the resin to generate heat, going back to one of the original uses of the resin.

2.2. BIO-BASED BINDERS, MODIFIERS, AND ADDITIVES

The NCHRP-IDEA project concept was to design a FPM produced with little-to-no virgin petroleum-based binder which implied the use of 1) high percentages of RAP and/or RAS, and 2) some type of non-petroleum based recycling agent (RA). Although RAP usage in paving applications became popular during the 1970s oil embargo, high-RAP FPM design has become more common due to increasing crude oil and aggregate costs, and environmental concerns, as discussed in Section 1.1.2. However, the design procedure is still evolving [53] [54] [55] [56]. RAS usage also began in the 1970s and continues to rise with a large increase in the utilization of asphalt shingles removed from roofs during maintenance or replacement (i.e. tear-off shingles) and from manufacturing waste [57]. The state of the art in FPM design using RAS, however, is still evolving [58].

FPM design using high percentages of RAP and/or RAS is a challenge unto itself and is leading to innovation. For example, new designs and construction of asphalt mixing facilities/equipment are occurring regularly that are marketed for the purpose of utilizing RAP percentages as high as 100% [59] [60] [61] [62]. Currently, the upper limit for RAP usage at Missouri FPM mixing facilities is about 50% with a more practical upper limit of 40%.

Although the use of guayule-based materials as components in FPMs is a unique concept, there are other instances of the investigation/use of other renewable and/or waste bio-materials as FPM binder or modifier. Early work on bio-based binder materials occurred in India where resin from the *Anacardium Occidentale* (cashew) tree was processed to be used as a RA [63]. Vegetable oils (virgin and waste) have been investigated extensively [64] [65], but a nonfood source is preferred for sustainable industrial applications. Pyrolysis is a thermochemical process that can efficiently generate bio-oils from bio-materials and has been used to investigate biomass (e.g. switchgrass) as a source for binder [66]. Liquefaction, also a thermochemical process, has been used to investigate swine manure as a source for binder [67].

Some proprietary RAs (e.g. Hydrogreen S and Evoflex CA) and warm-mix additives (added to lower the mixing temperature) are derived from tall oil, a paper manufacturing by-product [18] [19] [68] [69]. The tall-oil-based RAs are a large portion of the current state-of-the-art products used when high contents of RAP and/or RAS are utilized in FPMs.

The potential volumes of guayule resin that could be utilized as a FPM binder modifier are huge. A short discussion of those potential volumes is given in the Conclusions section.

3. LABORATORY INVESTIGATION

3.1. YULEX AND USDA-ARS ERA

The bulk of the work occurred between 2006 and 2014 during the NCHRP-IDEA Type 1 project. The project work was divided into three Tasks:

Task 1: Completion of administrative work; procurement of raw materials and equipment; development of equipment, laboratory infrastructure, and test protocols.

a. Significant quantities (unless indicated otherwise) of raw materials obtained for the project are as follows:
   - RAP1: obtained from Interstate 44 in Rolla, Missouri.
   - RAP2: obtained from a city street in Washington, Missouri.
   - RAS: processed tear-off roofing shingles (i.e. shingles removed from a roof) obtained from a local FPM producer.
   - USDA-ARS supplied chipped, whole-shrub guayule plant.
   - Yulex-supplied post-latex-extraction (PLE) guayule bagasse.
   - Yulex-supplied waste-stream guayule leaves and attached stems.
   - Yulex-supplied pelletized defoliated whole-shrub guayule plant.
   - Yulex-supplied pelletized waste-stream guayule leaves and stems (<50 lbs.).
   - Yulex-supplied pelletized PLE guayule bagasse (<50 lbs.).
   - Centrotrade-supplied (via Yulex) guayule latex (10 gallons).
   - Yulex-supplied dried latex.
   - Three different fractions of high-quality, crushed dolomite from a local quarry.

- Six different grades of polymer-modified and non-modified performance-graded (PG) binders.
- Two different, commercially-available, petroleum-based recycling agents: Cyclogen L from Tricor Refining, and Hydrolene H125T from HollyFrontier Refining.

b. Significant equipment/supply items purchased (or borrowed) are as follows:

  - Bohlin Gemini 150 Dynamic Shear Rheometer (DSR) and Cannon Instruments temperature probe.
  - Applied Testing Systems Bending Beam Rheometer (BBR) and 10 BBR beam molds.
  - Cox and Sons Rolling Thin Film Oven (RTFO), along with standard and large-lipped RTFO bottles.
  - Prentex Pressure Aging Vessel (PAV) and bottled, compressed breathable air.
  - 20 liter Oregon Environmental Systems Solvent Recovery Device (SRD) for large-scale primary distillations.
  - Clay-Gel Chromatography glassware, clay, and silica gel.
  - Large centrifuge for solvent extraction/recovery procedures.
  - Significant quantities of acetone, trichloroethylene (TCE), hexane, and lesser quantities of pentane, toluene, ethanol, and methanol.
  - Bottled, compressed carbon dioxide and nitrogen for gas purges during material recovery procedures.

- Buchi rotary evaporator and associated glassware/fixtures for final distillations/recovery. Note: this was borrowed from the Chemistry Department at Missouri S&T.

c. Equipment, laboratory infrastructure, and test protocols development included:

- Installation of an air compressor dedicated to the DSR, BBR, and RTFO.
- Fabrication/installation of a fume hood in an isolated room with an independent air-exhaust system: the solvent recovery device was installed under the fume hood, and the room served as an area to work with and store the solvents.
- Installation of compressed air lines and electrical power wiring/conduit for all new equipment.
- Fabrication of a required clean and dry air filtering system for the RTFO.
- Development of large-scale extraction and recovery procedures for RAP/RAS binders and guayule-based materials.

Task 2: Material characterization and binder-blending mixture experiments.

Task 3: FPM design, production, and testing.

3.1.1. Initial Project Activities: Task 1. Activities during the first quarter (three months) of the contracted performance period included finalizing administrative and legal issues, beginning the procurement of project materials and additional test equipment, establishing a panel of experts, and gathering literature for review. Regarding the project materials, investigations were undertaken to find the appropriate sources. Additional required testing equipment ordered during the first quarter included a RTFO and an assembly of glassware, etc. necessary to perform a clay-gel chromatography procedure for determining percent saturates and other properties of recycling agents. Bid specifications were written so that other necessary equipment could be put out on bid. These items included a DSR, a PAV, and a BBR. Individuals who agreed to serve on the expert panel are as follows:

- Dr. Peter Wu, Bureau Chief – Technical Assistance, Georgia Department of Transportation (Assistant to Georgine Geary, IDEA Program Technical Project Advisor).
- Joe Schroer, Field Materials Engineer, Missouri Department of Transportation.
- Dr. Katrina Cornish, Sr. V.P. R&D, Yulex Corporation.
- David Yates, Executive Director, Missouri Asphalt Pavement Association.

By the end of the first three quarters (nine months) of the project, a substantial portion of Task 1 had been completed:

- Modifications and/or installations of required electrical power, compressed air, and vacuum systems within the materials laboratories were undertaken.
- Two sources of RAP and one source of RAS had been secured and were being stockpiled in the laboratory.
- Some of the guayule feedstock had been obtained.
- Almost all equipment items had been delivered but not configured for use (e.g. the DSR and BBR).

The delay in full implementation of test equipment usage prompted the request for an extension of the performance period which was submitted and approved.

Individual tasks listed under Task 1 would continue to be completed as the project progressed. It was not until after the decision was made to generate guayule-based materials in the laboratory that Task 2 was started in earnest.

3.1.2. Material Characterization: Task 2, Part 1. Material characterization involved determination of material properties required to 1) select a minimum number of guayule-based extracts for further evaluation as recycling agents, 2) classify all petroleum- and potential guayule-based recycling agents, and 3) perform FPM design.

3.1.2.1 Extraction and recovery of guayule-based materials. A great deal of time at the start of Task 2 was dedicated to obtaining a guayule-based material with the properties required for use as a recycling agent (RA). Ultimately, eleven different combinations of guayule feedstock material, solvent(s), and extraction/recovery processes were investigated. The general criteria for a more in-depth evaluation of an extract were 1) similarity of the extract's temperature-viscosity relationship to those of commercially-available, petroleum-based RAs, 2) simplicity and relative safety of the extraction and recovery process, and 3) sufficient yield (weight percent of material recovered from a particular guayule-based feedstock).

The plant or plant-extract precursor materials investigated were three different plant feedstocks, two guayule-based materials resulting from the solvent extraction of one of the plant feedstocks, and the dried latex (bulk rubber). The plant feedstocks were USDA-ARS-supplied chipped whole-shrub (WS), and Yulex-supplied post-latex-extraction (PLE) bagasse (fibrous residue leftover after 90-95% of the high molecular weight rubber was removed), and waste-stream leaf and attached stems. The whole-shrub and waste-stream leaf/stem feedstocks were pulverized prior to solvent extraction using a horizontal shaft impactor. The PLE bagasse was already in a finely-macerated state. Figure 3.1 shows the guayule-based feedstock supplied by Yulex and USDA-ARS, and used for the greatest portion of the extractions.

The earliest acetone-extraction and recovery techniques of the guayule resin followed procedures outlined in the literature [11] [70]. The USDA-ARS supplied freshly harvested, whole-shrub guayule plants that had been field-dried, then run through a chipper and reduced to a size passing a 3/8 inch screen. The chipped whole-shrub was further reduced in size (-1/16 inch) using the horizontal shaft impactor. The pulverized guayule plant material was then soaked in acetone overnight with occasional stirring. The following morning, the acetone-resin solution was drained off, filtered, and stored in glass containers. A second soaking of the guayule plant material in acetone was performed but did not last as long as the primary soaking. The acetone-resin solution from the second soaking was, again, drained off, filtered, and stored in glass containers. A final wash of the guayule plant material with acetone was performed with a small amount of acetone and this wash solution was also filtered and stored in glass containers. The filtered solution was further clarified using the large centrifuge specified in the Abson binder recovery procedure, AASHTO T 170 [70]. The clarified acetone-resin solution (i.e. miscella) was recovered (i.e. desolventized) using the distillation equipment also specified in AASHTO T 170.

The quantity of recovered guayule resin using the method just described was minimal. Additionally, the Abson method of recovery was known to be somewhat dangerous in that, if not carefully watched, the material in the recovery flask could "bump" or "burp" and be violently discharged from the flask. Because the volumes of resin required for this study were so large, a 20 liter solvent recovery device (SRD) was, therefore, purchased. Figure 3.2 shows the SRD, the primary distillation device, and the rotary evaporator, the final distillation device, which were used for the remainder of the study. General extraction and recovery details for this scaled-up procedure are given in Appendix B.

Figure 3.1. Guayule Plant Feedstocks for Extractions

Screening the eleven different extracts for further evaluation was sometimes based simply on visual observation. For example, the first acetone-extracted resins from the chipped whole-shrub and the PLE bagasse would flow when slightly heated, and would “string out” (exhibit some cohesion and ductility) when pulled from the container with a small spatula, but would become stiff and/or brittle (glassy) upon cooling to room temperature. This behavior made these extracts ill-suited as a RA but demonstrated a potential to improve the high-temperature performance of FPMs as stiffening agents.

Primary distillation:
solvent recovery device

Final distillation:
rotary evaporator device

Figure 3.2. Primary and Final Distillation Stations

Simple acetone-extraction performed on the fibrous feedstocks was not producing a material suitable as a RA. The viscosity of these extracts did not indicate the potential for significantly reducing the viscosity of the RAP/RAS binders upon blending, which is the basic purpose of RAs.

The next step beyond simple acetone-extraction was determining the extent to which “maltene-like” oils and hydrocarbon compounds could be isolated from the acetone-extracted PLE bagasse resin. Buchanan et al. [71] present a method of performing acetone-extraction on whole plant material then partitioning the desolventized extractive into oil and polyphenol fractions using hexane (non-polar solvent) and aqueous methanol (polar solvent), respectively. The basic procedure outlined by Buchanan et al. was followed for this study but pentane was used instead of hexane to stay consistent with the standard clay-gel chromatography test for classifying recycling agents, which specifies pentane as the solvent [72]. Although the process outlined by Buchanan et al. involved whole plant material as the beginning feedstock, the PLE bagasse resin was investigated first because the PLE bagasse is a by-product of the rubber extraction process and finding a market for it would be most beneficial to the guayule processing industry.

The procedure, referred to as a liquid-liquid extraction, began with putting 100 grams of the acetone-extracted PLE bagasse resin into a large glass container then incrementally adding several hundred grams of a 90% aqueous methanol solution (90% methanol, 10% water, by weight) to the container while stirring with a glass rod. The aqueous methanol was added until no more resin (more specifically, the solids remaining in the container) would dissolve. At that point, pentane was added in measured increments while continuing to stir. When the stirring would stop, one could see a definite phase separation with the lighter density, light green colored pentane solution floating on top of the heavier, yellowish-orange colored aqueous methanol solution in the bottom of the container. The pentane addition and stirring continued until all solids had dissolved, except for a few solids that occupied the boundary layer between the two liquid phases. At this point, the majority of the pentane solution was siphoned into large glass jars and desolventized using the rotary evaporator device. Table 3.1 shows the viscosity test results for the recovered pentane solubles fraction of the acetone-extracted PLE resin.

Table 3.1. Viscosity Comparison for the Pentane Soluble Fraction of the PLE Resin

Temperature (°C)	Viscosity (centipoise)	
	Pentane Solubles	Cyclogen L (CycL)
60	1044	438
80	285	93
100	107	31

Table 3.1 shows the viscosity of the pentane solubles in comparison to that of Cyclogen L (CycL), a petroleum-based aromatic oil that is a marketed as a true rejuvenator, and was used throughout this study. The PLE resin pentane solubles are comparable to the CycL in viscosity and are also similar in that CycL is 98.2% pentane soluble (as determined during clay-gel absorption chromatography, to be discussed later). Generating and utilizing the pentane solubles from the guayule materials is the preferred route to obtaining a bio-based, plant-oil-type RA. However, the extraction and recovery process is more complicated, and yield would be considerably smaller on a weight-percent basis of the guayule feedstock. This small investigation yielded approximately 15 grams of pentane solubles from the 100 grams of PLE bagasse resin. This particular PLE resin batch was actually recovered from the small batch of PLE bagasse obtained early in the study. Acetone-extraction was performed on five kilograms of dried PLE bagasse.

Therefore, the pentane-soluble yield using the liquid-liquid extraction procedure was only 0.3% of the dried PLE bagasse feedstock.

The focus returned to single-solvent extractions. The following is a list of the various guayule plant feedstocks and the solvents used for extraction:

- Pulverized whole-shrub: pentane.
- PLE bagasse: toluene, pentane, and hexane.
- Pelletized waste-stream leaf/stem: acetone, to see how it compared to whole-shrub and PLE bagasse acetone-extracts.
- Pulverized waste-stream leaf/stem: hexane.

Because they are essentially waste products (potential co-products) of the latex extraction procedure used by Yulex, the PLE bagasse and the waste-stream leaf/stem materials were the primary feedstocks of interest.

The toluene-extracted resin from the PLE bagasse had viscous properties similar to the acetone-extracted PLE bagasse resin (very stiff), but was slightly less temperature susceptible (i.e. exhibits less change in viscosity for an equal change in temperature). The pentane-extracted resin from the PLE bagasse and the WS possessed viscous properties more appropriate for a recycling agent but pentane is very volatile and dangerous, and expensive. The hexane-extracted resins of both the PLE bagasse and waste-stream leaf/stem materials were similar to the PLE bagasse pentane-extracted resin in terms of viscosity. The hexane-extraction of the PLE bagasse resulted in a 3.0% yield of resin based on the oven-dry (60°C overnight) weight of the bagasse, and the hexane-extraction of the pulverized waste-stream leaf/stem feedstock resulted in a 5.1% yield of resin (LF), also based on the oven-dry (60°C overnight) weight of the leaf/stem feedstock. Because hexane has the advantage of being less dangerous and less expensive than pentane, hexane became the primary solvent to be further evaluated.

In an effort to improve upon the liquid-liquid extraction procedure discussed earlier, a method used in the “essential oil” production industry was investigated to obtain more of the non-polar compounds present in guayule feedstocks [73]. The basic methodology begins by extracting the non-aromatic waxes, pigments, and volatile aromatic molecules from the feedstock using a solvent, usually hexane. The solvent is then recovered through distillation leaving a resin (or a “concrete” in essential oil parlance). The waxy materials and “essential oils” in the resin are further separated with an alcohol (e.g. pure ethanol) while warming and stirring the resin/alcohol mixture. The aromatic oils (or the “absolute” in essential oil parlance) and some waxy compounds are dissolved by the alcohol while the majority of the waxy materials remain as a residue. The alcohol solution is then repeatedly cooled and filtered to remove the few dissolved waxy compounds. The alcohol is then recovered through distillation leaving the aromatic or “essential” oils.

For the initial investigation into this method, 50 grams of the hexane-extracted resin (LF) from the pulverized waste-stream leaf/stem feedstock was put in a glass beaker and ~1 liter of pure ethanol was added to the beaker. The beaker was then put on a hot plate and warmed (somewhat below the boiling point of ethanol which is 79°C) while stirring with a glass rod. It could be visually observed that separation was occurring as the ethanol took on a greenish color and the residue in the bottom of the beaker became very sticky. The ethanol/oil solution (miscella) was decanted into a separate container and the residue was covered with another liter of pure ethanol to assure maximum removal of the oils. This second liter remained clear after a lengthy interval of warming and stirring indicating that the greatest majority of the ethanol-soluble compounds had been removed with the first liter.

The ~2 liter bottle of ethanol miscella was put in a refrigerator at a temperature of ~ 35°F (~ 2°C) overnight then cold-filtered through coffee filters the following day. Several filters (typical mesh size is 10 – 15 micrometers) had to be used because there was a significant amount of waxy material precipitate present in the cooled miscella. The filtered miscella was then put in a freezer at ~ -20°F (~ -30°C) overnight then cold-filtered the next day, removing a smaller, but significant, amount of precipitates. The process of cooling and filtering was repeated one more time using the freezer. The ethanol was then removed through distillation using a rotary evaporator and the recovered residue was collected for future testing.

Based on the first attempt at partitioning of the “oil” (ethanol-soluble) portion of the LF extract, the yield was 54.4 % of the weight of the LF. Therefore, based on the 5.1% yield of the LF extract from the pulverized leaf/stem feedstock, one would estimate a 2.8% yield of the LF oil based on the weight of the pulverized leaf/stem. This was a big improvement over the 0.3% pentane soluble material yield from the dried PLE bagasse, as described earlier. The ethanol partitioning method was simpler, safer, produced more material, and said material had viscous properties that were more appropriate for use as a RA, relative to the acetone-extracted resins.

Ultimately, however, the ethanol partitioning of the LF extract was not pursued further. The decision was made to focus on the LF material as extracted from the waste-stream leaves and attached stems. The extraction procedure was simple and the yield averaged 4.4% by weight of the oven-dry (60°C) waste-stream leaf/stem. The LF was dark-green in color, semi-solid at room temperature, and had a piney, pleasant odor. However, the LF also contained some natural rubber which increased the tackiness of any blend in which it was present.

Soon after beginning testing using the LF extract, the Yulex Corporation suggested acetone-extraction on the dried latex (bulk rubber) they produced as a secondary product. The rubber had residual, amber-colored resin in it that 1) was undesirable for producing a near-white rubber that enables the creation of various grades of rubber, and 2) could be extracted using acetone. Yulex supplied about 50 pounds of the rubber and a method was devised to extract the resin by cutting the rubber into approximately 2 inch cubes, freezing the cubes in liquid nitrogen, pulverizing the frozen cubes, soaking the flaked rubber in acetone for an extended period of time, then desolventizing the acetone-resin solution in a two-step distillation process. The acetone-extracted rubber resin (RR) was amber in color, flowed at room temperature, and had a slightly pungent, but not unpleasant odor. The acetone-extraction process was relatively simple and the yield averaged about 13% by weight of the rubber. The procedural details are given in Appendix B.

After months of experimentation, the LF and RR were chosen for further evaluation. Each of the two guayule-based materials was compared to an appropriate petroleum-based product of similar viscosity: 1) RR was compared to CycL, and 2) the LF was compared to a PG52-28 binder. PG52-28 is a soft binder often used in FPMs with high contents of RAP and/or RAS, and in circumstances where the contract-specified binder grade is stiffer than PG52-28. Table 3.2 shows a summary of results, in a general chronological order from top to bottom, of the investigations into obtaining a guayule-based extract that could serve as a RA.

Table 3.2. Summary of Initial Guayule-Based Material Generation Investigations

Plant or Plant Extract Precursor Materials	Solvent	Results
Whole-Shrub (WS)	Acetone	The WS resin is much stiffer and more temperature susceptible than a PG52-28 binder.
PLE Bagasse (PLE)	Acetone	The PLE resin is very stiff. Viscosity-temperature relationship similar to RAP binders.
Waste-Stream Leaf/Stem	Acetone	Visual inspection only. Visual observation was similar to acetone-extracted WS resin. Too glassy (brittle) at room temperature.
Acetone-extracted PLE Bagasse Resin	Pentane-Aqueous Methanol Liquid-Liquid Extraction	The extract has good viscous properties comparable to Cyclogen L. No follow-up work: pentane hazard-risk and high cost, and a very complex production method. Very small yield.
Whole-Shrub (WS)	Pentane	Visual inspection only. The extract demonstrates moderate ductility, high elasticity. No follow-up work: pentane hazard-risk and high cost.
PLE Bagasse (PLE)	Pentane	Visual inspection only. The extract demonstrates moderate ductility and elasticity. No follow-up work: pentane hazard-risk and high cost.
PLE Bagasse (PLE)	Toluene	The resin is similar to the acetone-extracted PLE resin in terms of viscosity but is slightly less temperature susceptible.
Waste-Stream Leaf/Stem	***Hexane***	***The extract (LF) has viscosity similar to a PG52-28 but is significantly less temperature susceptible. Simple production method and moderate yield. Demonstrates high ductility, moderate elasticity upon visual inspection. Contains some rubber and is tacky.***
PLE Bagasse (PLE)	Hexane	The extract has a viscosity-temperature relationship similar to the LF material with higher viscosity; i.e. too stiff.
Hexane-extracted LF	Cold-filtered Ethanol-partition	The extract is less viscous than a PG46-28 binder but more viscous than Cyclogen L, and more temperature susceptible. Production less complex than pentane-aqueous methanol partitioning. Small yield
Dried Latex (bulk rubber)	***Acetone***	***The rubber resin (RR) has viscosity similar to Cyclogen L but is slightly less temperature susceptible. Relatively simple production method and high yield.***

Note: Italicized materials chosen for further investigation

3.1.2.2 Raw material descriptions. RAP1 came from a Missouri Department of Transportation (MoDOT) project on Interstate 44 in Phelps County, Missouri. RAP2 came from a city street project in the city of Washington, Missouri. The rationale for the selection of two different RAP materials was based on the early idea of evaluating RAPs of significantly different quality. If RAP comes from a source other than a state roadway, MoDOT requires additional testing on the recovered RAP aggregates, specifically, the Micro-Deval test. Micro-Deval is an aggregate durability test that measures resistance to abrasion in the presence of water [74].

The RAPs were first processed in the laboratory by shaking them across a ¾ inch screen, running the +¾ inch material (retained on the ¾ inch screen) through a horizontal-shaft impactor, then running the pulverized RAP through the ¾ inch screen again such that the sample used for obtaining test specimens contained only RAP that had passed through the ¾ inch screen.

The RAS was supplied by a local asphalt contractor and had already been processed such that it would pass the ½ inch screen. However, MoDOT's specification for RAS is that it must pass the ⅜ inch screen. Therefore, the RAS was processed in the laboratory in the same manner as the RAP such that the sample used for obtaining test specimens contained only RAS that had passed through the ⅜ inch screen.

Virgin aggregate used in the FPMs was a dolomite from the Gasconade formation, obtained from a local asphalt producer. Three different size fractions were obtained: ½ inch clean, ⅜ inch clean, and manufactured sand.

The origins and basic methodology for processing of the precursor materials for the LF and RR materials were discussed in the previous section.

3.1.2.3 RAP/RAS binder contents and guayule-based extract yields.

Procedures ultimately used for solvent-based extraction and recovery for the RAP/RAS binders, and the RR and LF materials were based on guidance given in standard test methods and in the literature [11] [70] [75] [76] [77]. However, due to the amount of material needed to perform the required testing, certain aspects and/or portions of the standard test procedures were combined to develop the procedures utilized. The evolutionary development of the procedures that were eventually used account for a large portion of the time dedicated to this project. Detailed extraction and recovery procedures are in Appendix B for the guayule-based materials and Appendix C for the RAP and RAS binders. Recovery (yield) results are given in Table 3.3.

Before the procedures used to generate the data in Table 3.3 were fully developed, binder contents (or more correctly, percent losses) of the RAP/RAS were first determined using a standard solvent-extraction method, AASHTO T 164 [75], and the binder ignition oven based on AASHTO test method T 308 [78]. Results are given in Table 3.4.

The RAP1 and RAS binder content results in Table 3.3 (determined using the project-developed extraction/recovery methods) relative to the T 164 results in Table 3.4 compare fairly well. However, the results for RAP2 in Table 3.3 ran somewhat higher than those in Table 3.4.

The deltas (differences) between T 308 and T 164 shown in Table 3.4 are large. The differences are primarily due to a combination of factors:

- Aggregate mass loss in the T 308 test results; largest contributor to deltas.
- Incomplete binder extraction in T 164 (aggregates absorb binder to differing degrees and the extent of solvent-removal of said binder varies).

- Burning of small amounts of paper, plastic, and wood included in the RAS that show up as a mass loss in T 308.

Table 3.3. Solvent-Based Extraction/Recovery Yield Results

Material	**Batch ID**	**Amount Recovered (gm)**	**Content or Yield (%)**	**Mean (%)**	**St. Dev. (%)**
Acetone-Extracted Guayule Rubber Resin (RR)	RR-1	226.6	11.5	11.9	0.30
	RR-2	247.0	12.2		
	RR-3	237.6	11.8		
	RR-4	248.2	12.0		
	RR-5	301.3	14.6	14.0	0.45
	RR-6	410.5	13.9		
	RR-7	312.5	14.0		
	RR-8	339.8	13.5		
Hexane-Extract from Waste Stream Guayule Leaves and Attached Stems (LF)	LF-1	215.9	4.5	4.5	0.09
	LF-2	210.4	4.4		
	LF-3	219.4	4.6		
	LF-4	211.2	4.4		
	LF-5	212.0	4.4		
RAP1 Binder (State Hwy Material: -3/4″)	RAP1-1	478.6	4.8	4.8	0.07
	RAP1-2	482.0	4.8		
	RAP1-3	492.3	4.9		
	RAP1-4	492.5	4.9		
	RAP1-5	512.1	4.8	4.7	0.14
	RAP1-6	488.6	4.7		
	RAP1-7	492.4	4.7		
	RAP1-8	462.1	4.5		
RAP2 Binder (Municipal Street Material: -3/4″)	RAP2-1	550.3	5.5	5.4	0.03
	RAP2-2	547.1	5.5		
	RAP2-3	543.3	5.4		
	RAP2-4	541.7	5.4		
	RAP2-5	558.8	5.5	5.5	0.01
	RAP2-6	569.1	5.5		
	RAP2-7	562.2	5.4		
	RAP2-8	559.1	5.5		
RAS Binder (-3/8″)	RAS-1	465.1	22.8	22.8	0.08
	RAS-2	468.7	22.9		
	RAS-3	459.8	22.7		
	RAS-4	459.8	22.8		

NOTE: The binder contents of the RAPs and RAS, and the yields of the LF material are based on the weight of the material after drying/warming overnight at 60°C. Yields of the RR material are based on the weight of the air-dry rubber subjected to acetone-extraction. Batches 1 – 4 (and LF batches 1 – 5) were extracted much earlier than batches 5 – 8.

Table 3.4. T 164 and T 308 Binder Contents

Material	RAP1			RAP2			RAS		
Test/Delta	T 164	T 308	Delta	T 164	T 308	Delta	T 164	T 308	Delta
Trial-1 (%)	4.92	7.19	2.27	5.24	6.14	0.90	23.2	26.4	3.25
Trial-2 (%)	5.06	6.99	1.93	5.08	6.33	1.25	22.0	26.5	4.52
Mean (%)	4.99	7.09	2.10	5.16	6.24	1.08	22.6	26.5	3.89
StDev (%)	0.10	0.14	0.24	0.11	0.13	0.25	0.84	0.06	0.90

The delta for RAP2 is considerably smaller than RAP1. This could be due to the fact that RAP2 contained limestone and some trap rock, a hard, low-absorption aggregate used in many Missouri street resurfacing projects. The smaller RAP2 delta relative to RAP1 could also be due to the fact that RAP1 contained dolomite; i.e. limestone with an elevated magnesium level. Dolomite is a common Missouri mineral that can experience excessive mass loss that increases with increasing ignition oven test temperatures.

The temperature for binder ignition oven testing of the reclaimed materials should be the same as that used during binder ignition testing of the production FPM [79]. However, because no FPM production had occurred prior to generating the T 308 data in Table 3.4, the binder ignition testing of the RAPs and RAS was performed at 538°C, the default temperature specified in T 308.

3.1.2.4 RAP/RAS aggregates gradations. Gradation analyses [80] [81] were performed on the recovered RAP and RAS aggregates from both the AASHTO T 308 and AASHTO T 164 procedures used to develop the results in Table 3.4. Gradation, or particle size distribution, is necessary for FPM design. The gradation results are given in Table 3.5.

Table 3.5. Gradation Results for Recovered RAP/RAS Aggregates

Material	RAP1		RAP2		RAS	
Recovery Method	Solvent	Ignition	Solvent	Ignition	Solvent	Ignition
Sieve Size	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass
¾ in. (19.0mm)	100	100	100	100	100	100
½ in. (12.5mm)	97	96	100	100	100	100
3/8 in. (9.5mm)	90	91	98	98	100	100
#4 (4.75mm)	69	71	75	74	99	99
#8 (2.36mm)	50	52	50	49	97	97
#16 (1.18mm)	40	42	36	36	81	81
#30 (600µm)	33	34	28	27	59	57
#50 (300µm)	25	27	19	18	51	50
#100 (150µm)	15	16	13	12	45	44
#200 (75µm)	9	10	11	9	37	35

The difference between the solvent- and ignition-recovered-aggregate gradations in Table 3.5 is small, but there is some evidence that the RAP1 dolomite breaks down more than the RAP2 and RAS aggregates during ignition testing. For FPM design, the gradations of the solvent-recovered RAP/RAS aggregates from the Table 3.3 extractions were assumed to be the same as the average of the solvent- and ignition-recovered-aggregate gradations in Table 3.5. Although not required for FPM design, the RAS fiber content was determined to be approximately 0.5% by weight of the RAS as a consequence of the washed sieve analysis of the recovered RAS aggregates.

3.1.2.5 Recycling agent classification. To properly perform FPM design that includes reclaimed binders, standard practice calls for classification of materials intended to be used as recycling agents. To this end, a standard material specification, AASHTO R 14 [82], is being referenced. The specification calls for several properties to be determined: viscosity, flash point, viscosity ratio (based on thin film oven (TFO) or rolling thin film oven (RTFO) residue viscosity relative to the original viscosity), weight (mass) change, specific gravity (relative density), and percent saturates. Table 3.6 summarizes all test results for recycling agent classification.

Table 3.6. Recycling Agent (RA) Classification Results

Property or Parameter	LF	PG52-28	RR	CycL
RTFO viscosity @ 60°C (centipoise)	21450	160000	618	624
Original viscosity @ 60°C (centipoise)	36750	62125	218	438
Viscosity ratio (RTFO/original): maximum = 3	0.6	2.6	2.8	1.4
AASHTO R 14 RA Classification	RA 250↔500	NA (>RA 500)	RA 5	RA 5
Flash Point (°C): minimum = 218°C	~200	Not Determined*	213**	254***
Saturates (weight %): maximum = 25%	11.26***	Not Determined*	1.08***	16.38**
Weight (mass) change (%): maximum = ±4% for RA1 and RA5, ±3% for all others	-8.475	-0.066	-11.065	-1.817
Specific gravity (to be reported: no specification limits)	1.003	1.012	1.015	1.004

NA = Not applicable; *Details in following discussions; **Average based on two replicate tests; ***Based on testing only one specimen

- Percent Saturates (Clay-Gel Absorption Chromatography Testing).

According to AASHTO R 14, saturates are limited to a maximum of 25% (or 30% if all other specified criteria are met) and are to be determined using the clay-gel absorption chromatographic test method ASTM D 2007 [72]. From this standardized test, one can determine the quantity of four different hydrocarbon types and structural groups in the recycling agent: saturates, aromatics, polar compounds (or polar aromatics), and asphaltenes (n-pentane insolubles). The relative proportions of these four groups affect the properties of the petroleum-based binder, and presumably, any blend of a guayule-based material and petroleum-based binder.

Clay-gel chromatography was performed on the RR, LF, and the CycL. Although the PG52-28 binder was used as a recycling agent in this study, clay-gel chromatography testing on the PG52-28 binder was not deemed necessary because it does not technically fall within the purview of R 14.

As shown in Table 3.6, all materials tested for percent saturates meet the criteria specified in AASHTO R 14 in that they are below 25%. Although not shown in Table 3.6, the LF and RR have a much higher polar compound content and considerably smaller aromatic compound content than the CycL. In a petroleum-based binder, age-hardening is a process by which the polar and aromatic compounds, over time, oxidize and become asphaltenes which are very large, complex molecules (i.e. microscopic solids) that serve as a bodying agent in the binder. Therefore, blends containing the LF or RR (both with higher polar compound contents than CycL) could possibly have an increased rate of age-hardening relative to blends with CycL.

Saturates (also known as paraffins) serve as non-solvents or a gelling agent in a colloidal system in which the asphaltenes are dispersed or peptized by the polar compounds (also known as nitrogen bases), and the aromatics (also known as first and second acidaffins) serve as a solvent for the dispersed asphaltenes [83] [84]. Figure 3.3 shows the clay/gel percolation column chromatography test setup.

Preparation of clay-gel (left) and clay (right) columns

Clay-gel percolation columns stacked and loaded with pentane-soluble solution

Figure 3.3. Clay-Gel Absorption Chromatography Test Setup

- Mass Change.

Mass change testing of the LF, RR, CycL, and PG52-28 was conducted using the rolling thin film oven (RTFO) method AASHTO T 240 [85]. The results are presented in Table 3.6.

The mass change (loss in this case) for the RR and LF materials exceeds the maximum allowable (4%) for any class of recycling agent (RA) based on AASHTO R 14 specifications. The PG52-28 and CycL met the specification. However, it should be noted that AASHTO R 14, as well as most every specification referenced for this research, pertains to petroleum-based binders, not necessarily a bio-based alternative.

Mass change testing occurs at 163±1°C. Some of the chemical compounds in the guayule-based materials are terpenes, compounds with isoprene molecules (C_5H_8) as the basic building block. Gas chromatography – mass spectrometry (GC-MS) test results (presented later) show some of the volatile compounds present in the RR and LF materials. Although these compounds are volatile and, even though they may have high boiling points in their pure form (terpenes especially), they have low flash points.

- Specific Gravity (Relative Density).

AASHTO T 228 [86] was followed in performing specific gravity tests on the PG52-28, CycL, RR, and LF materials. The guayule extracts required removal of a significant amount of gas bubbles prior to determining the specific gravity at 25°C. This aspect of the resins was not surprising in that they had just been recovered using the rotary evaporator which unavoidably whips gas into the recovered material.

Figure 3.4 shows the images of before and after a soft brushing of the surface of the RR with a propane torch. One can clearly see small bubbles in the RR in the pycnometer on the left. Care was taken to do as little as possible in regard to reheating the RR in order to facilitate the removal of the bubbles but not drive off any lighter compounds thereby altering the specific gravity of the original extract. The image on the right shows the final state of the RR in the pycnometer just prior to specific gravity testing. The results are presented in Table 3.6.

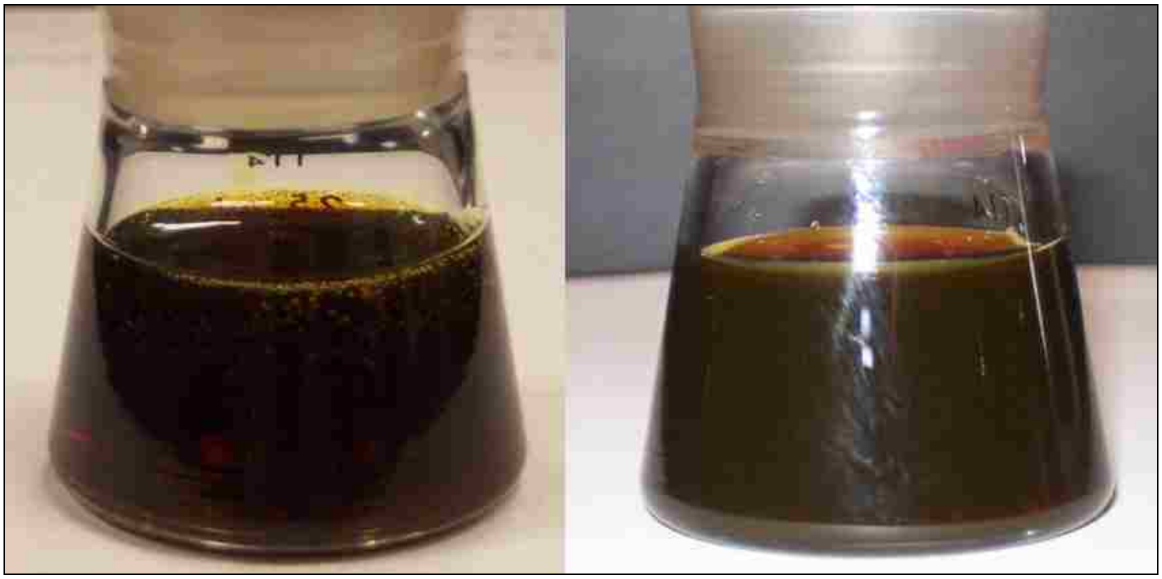


Figure 3.4. RR Specific Gravity Testing

- Viscosity and Viscosity Ratio.

A Brookfield rotational viscometer was used to determine viscosity-temperature relationships per AASHTO T 316 [87]. Note that this is a deviation from specifications in AASHTO R 14 which calls for viscosity testing at 60°C using AASHTO T 201 or T 202 and then reporting the results in the “stoke” unit of viscosity. The stoke is equal to the poise (viscosity units determined using T 316) divided by the density (specific gravity) of the liquid. However, because the density or specific gravity of the petroleum-based binders and guayule-based materials are very nearly 1.0, stoke and poise values are very nearly the same. Therefore, because R 14 classifications are based on a range of viscosity, and because the calculated viscosity ratio is not dependent on the actual viscosity unit used, viscosity results shown in Table 3.6 are given in centipoise. The results given in Table 5 show that all four materials meet the viscosity ratio specification in R 14. Figure 3.5 shows the Brookfield viscometer.

Figure 3.5. Brookfield Viscometer

The RA classifications in Table 3.6 line up fairly well between the materials that were compared. Both the RR and the CycL are classified as RA 5, but the LF and PG52-28 classifications are somewhat different. It is important to remember, however, that the classifications are based on viscosity at only one temperature. Viscosity measurements at more temperatures for each material will be presented later in the report, and the reason will become clearer as to why PG52-28 was chosen as the comparative petroleum-based binder to the LF material.

- Flash Point.

Flash point testing is required as a safety issue and was performed per AASHTO T 48 [88]. As shown in Table 3.6, the LF and RR materials did not meet the flash point specification in AASHTO R 14, but they did not fail by a large margin. In fact, the margin of failure of the LF (~18°C) was essentially the same as the multi-laboratory precision d2s (i.e. reproducibility) value of 18°C, and the margin of failure of the RR (5°C) was less than the single operator precision 1s (i.e. repeatability) value of 8°C. As discussed in earlier reports in regard to the large mass loss (volatilization) experienced by the guayule-based materials during heating at typical FPM mixing temperatures, it may be necessary to pre-condition or modify the processing of the guayule-based materials to make them more thermally stable and reduce the mass loss. This action would also, presumably, increase the flash point. Testing of the PG52-28 binder was not performed because it was assumed that the flash point would be higher than that of the CycL which has a flash point of 254°C, well above the specified minimum of 218°C. Figure 3.6 shows the flash point test setup.

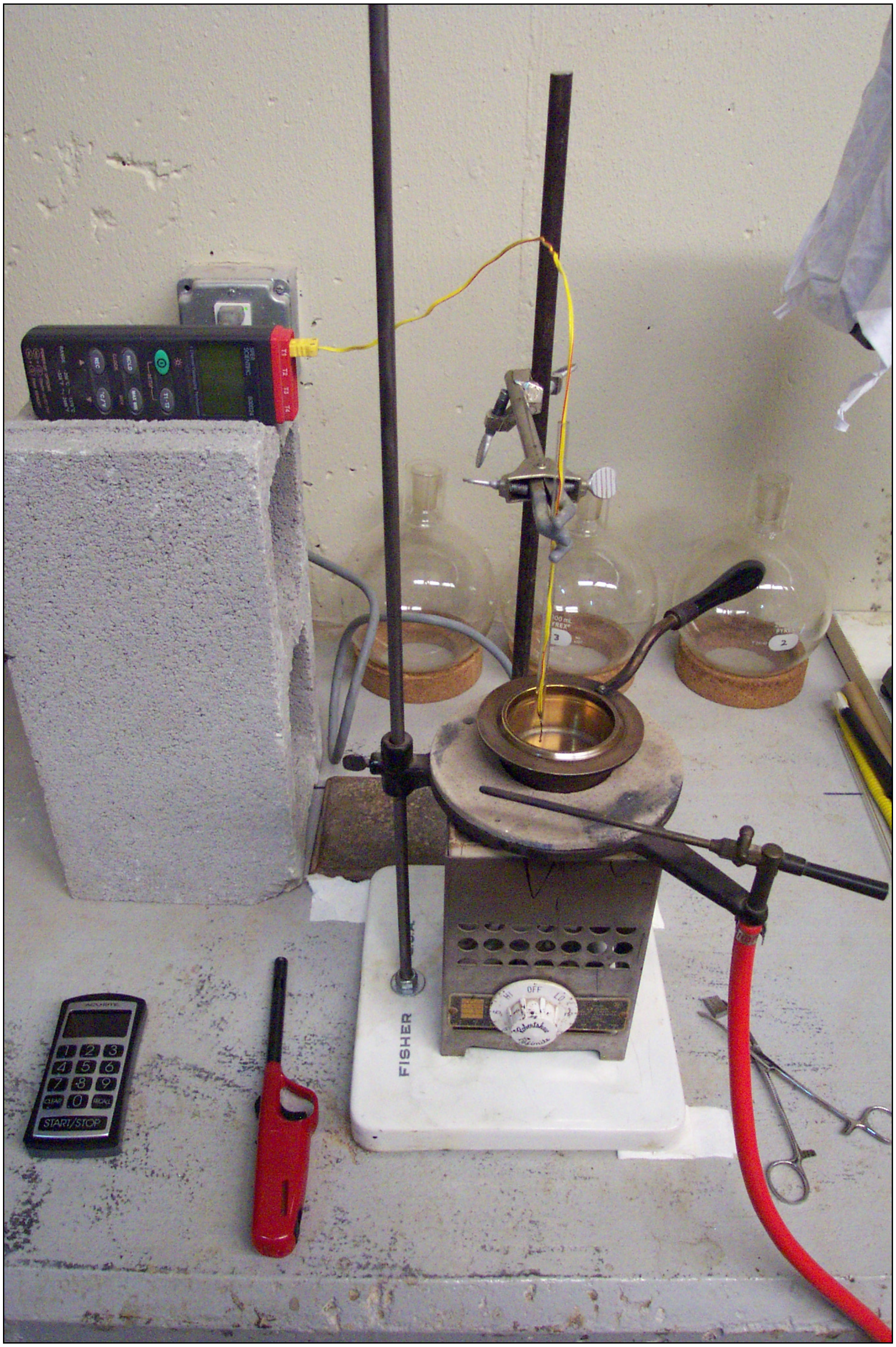


Figure 3.6. Flash Point Test Setup

3.1.2.6 Gas chromatography – mass spectrometry (GC-MS). The general intent of GC-MS testing was to evaluate the efficiency of the hexane and acetone desolventization process. Identification of major volatiles in the RR and LF materials was also of interest. The identification method used is called "headspace sampling using solid phase micro-extraction (SPME) with gas chromatography mass spectrometry (GC-MS)" (39). The media that was used to sample the guayule-based materials was a polydimethylsiloxane (PDMS) SPME fiber. The testing was done in collaboration with colleagues in the Environmental Engineering section of the Department of Civil, Architectural, and Environmental Engineering at Missouri S&T. Tests were performed on an operator-availability basis and not all variables (e.g. specimen size) were carefully controlled. The results are shown in Figure 3.7.

The gas chromatography (GC) device has a 28 minute long heating profile (x-axis on each chromatogram is time in minutes). At initiation (time = 0), the temperature in the GC chamber is 35°C and remains so for 5 minutes. The temperature then begins to ramp up at 15°C per minute for 13 minutes and then holds at 230°C for the remaining 10 minutes. The y-axis is the "abundance," or sometimes referred to as "intensity" of the compound detected.

The acetone and hexane levels (labeled low and to the left in the appropriate chromatogram) indicate that the desolventization procedures were very good at removing the solvents. Many of the compounds identified in Figure 3.7 are terpenes, compounds that have the isoprene molecule (C_5H_8) as the basic building block. Terpenes are mostly single-digit multiples (n) of the isoprene unit $(C_5)_n$ which builds up the carbon skeleton. The monoterpenes (i.e. two isoprene units or $C_{10}H_{16}$) α- and β-Pinene, and Limonene, are very interesting in that they are natural solvents. Pinenes are the basic compounds in turpentine while Limonene is used extensively in “citrus” cleaners. This capacity to serve as a solvent or degreaser is what makes certain guayule-based extracts attractive. They could be used as pre-treatment additives to RAP/RAS to help soften the hardened binder prior to FPM production thus improving the blending of reclaimed and virgin binders. The original USDA-supplied de-rubberized resin also had high monoterpene levels. It was the Pinenes that one could smell upon the first opening of the gallon can.

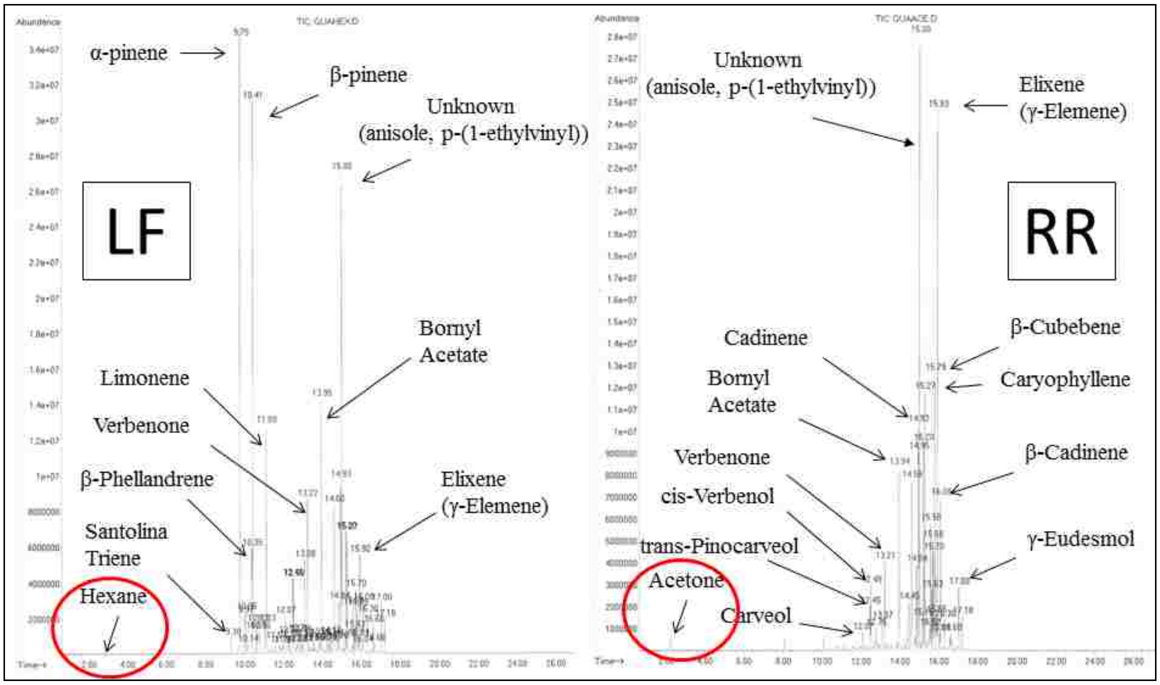


Figure 3.7. Chromatograms of LF (left) and RR (right) Materials

Other compounds identified in Figure 3.7 are sesquiterpenes (C_{15}), diterpenes (C_{20}), or triterpenes (C_{25}). Some of the compounds may have isoprene structures with some functional groups attached, which case they are referred to as terpenoids. Many terpenes are sometimes referred to as essential oils (e.g. Pinenes, Limonene, Caryophyllene, Cadinene, and Santolina Triene) (?). The mass spectrometry software indicated uncertainty when identifying the peak labeled as unknown, and generated a "best guess" which is the compound in parenthesis. It is not unusual for compounds to be inaccurately identified or they may be real and have been formed as reactions of other compounds in the feedstock material during the GC procedure.

3.1.2.7 Viscosity testing. AASHTO T 316 [87] was used for the viscosity testing presented in this section. Figure 3.8 shows the viscosity results for the original (not-RTFO-aged) RAP1, RAP2, RAS, PG52-28, and PG46-28 binders. The PG46-28 was included because at the time these tests were performed, it was not clear which petroleum-based binder(s) would be utilized in a comparative analyses.

Figure 3.8 shows three distinct groupings of material viscosities. The lowest viscosity group includes the three virgin (original) commercially-available binders, in ascending order of greater viscosity: PG46-28, PG58-28, and PG64-22. The next group has higher viscosities as expected: the two RAPs. The third material is the RAS, and as expected, the $\text{RAS}_{\text{(orig)}}$ binder is much more viscous than any of the other materials. As a pure blend (i.e. a non-blended material), the mixing temperature is ~265°C (~510°F) meaning its presence in a blend in any proportion will raise the mixing temperature of that blend, relative to what it would be without it. The Asphalt Institute has published recommended mixing and compaction viscosities for FPMs. The recommended binder viscosity for FPM mixing is 0.17 ± 0.02 Pa·sec or 170 ± 20 centipoise [90], as shown by the dashed lines in Figure 3.8.

The choice of comparing the RR to the CycL and the LF to the PG52-28 was based on their relative viscosity-temperature relationships. It seemed to be the only parameter that could logically be used as a basis of comparison because the reduction of viscosity of the hardened binder in the RAP/RAS is a primary reason for utilizing a RA. The viscosity results for these comparisons are given in Figure 3.9.

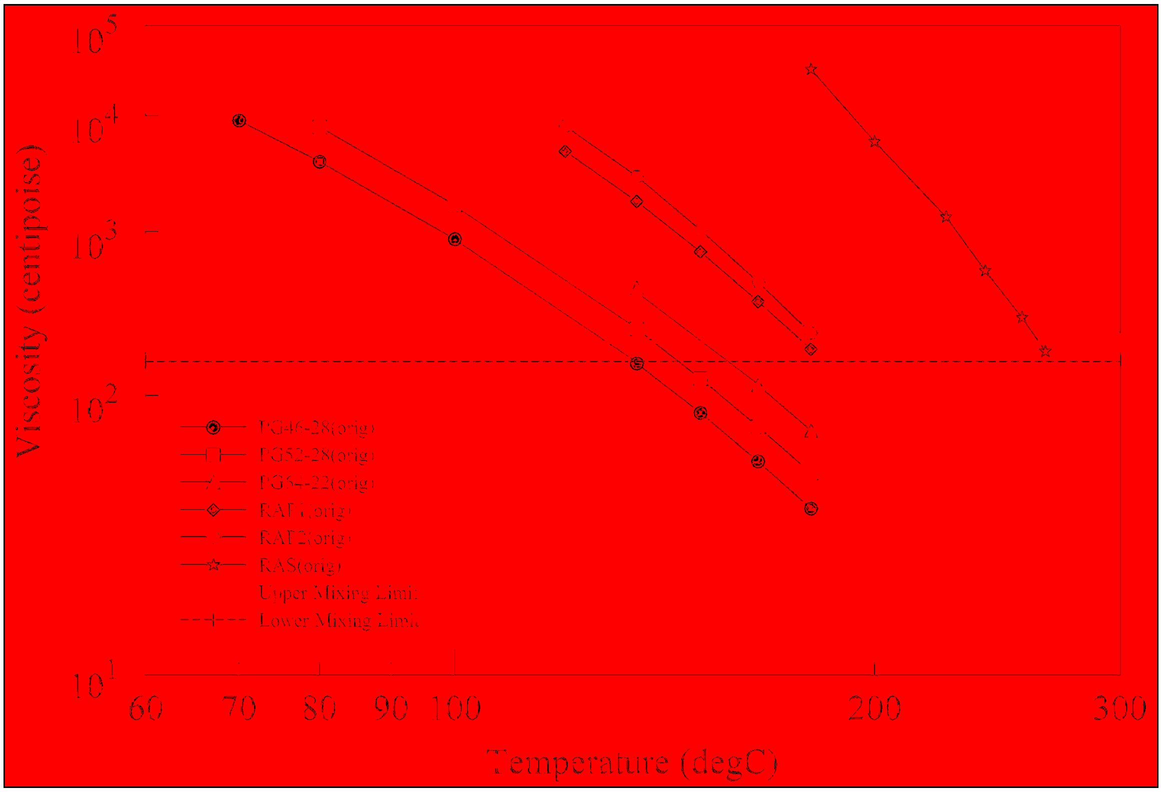


Figure 3.8. RAP, RAS and PG Binder Viscosities

There are two significant features about the curves presented in Figure 3.9. One is the difference in the slopes for the LF and PG52-28 materials, both original and RTFO-aged. The slope of a viscosity-temperature curve shows a material's temperature susceptibility which is the change in viscosity for a given change in temperature. Low temperature susceptibility is desirable in a binder material and the LF material is superior to PG52-28 in this respect across the entire temperature range in which they were tested. Also, the relative location of the LF and PG52-28 curves shows why these two materials were chosen to be compared; they are fairly similar over a wide range of temperatures. The original and RTFO-aged RR and CycL are also very similar in terms of viscosity and the RR shows a slight advantage in temperature susceptibility over the CycL.

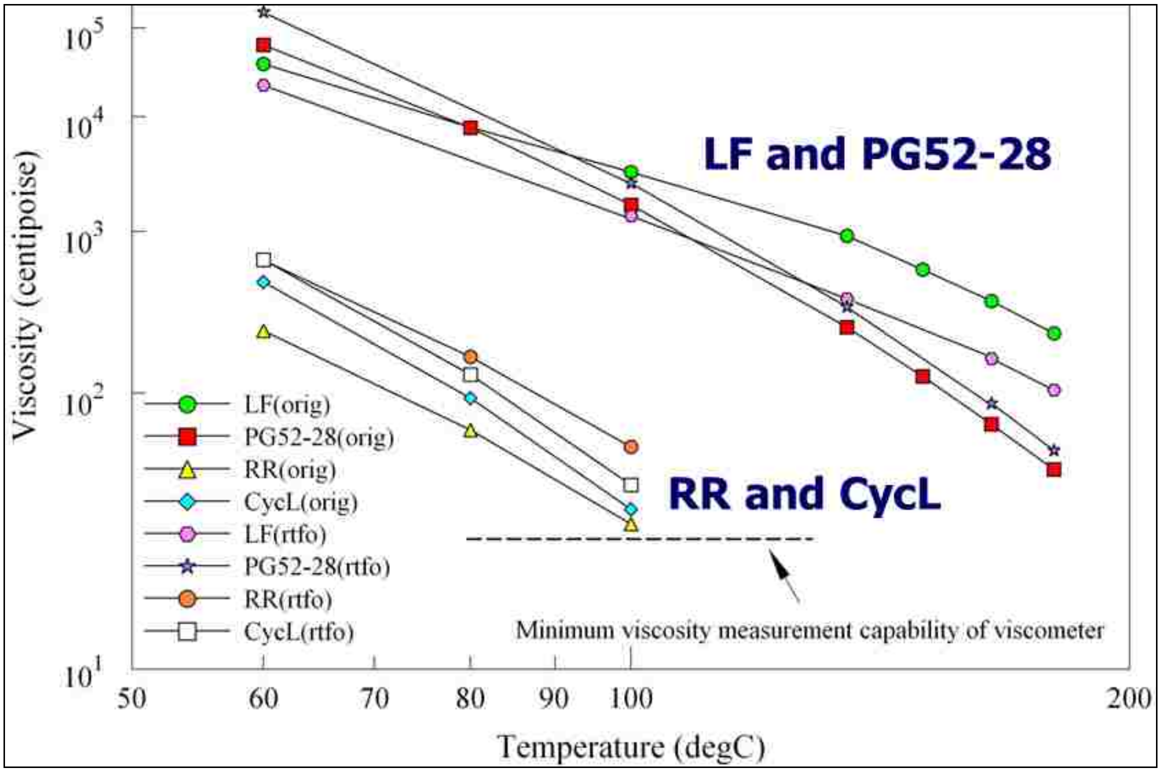


Figure 3.9. Comparison of Viscosity-Temperature Relationship

The second significant feature in Figure 3.9 is the viscosity reduction of the LF upon RTFO-aging. This behavior runs counter to that of petroleum-based binders. During viscosity testing on the original LF, it became apparent that at a temperature somewhere around 150°C, the LF was undergoing changes as indicated by erratic viscosity readings during spindle rotation. Upon closer inspection, it was observed that large bubbles were appearing on the surface of the specimen soon after a spike in the viscosity reading. The viscosity of the LF was lowered after shearing at elevated temperatures. It is unclear why this occurred but degradation or de-polymerization of the rubber (polyisoprene) molecules could be the cause. This behavior also gave an indication that there may be issues with mass change for this material, which proved to be the case.

The RR, on the other hand, behaves typically in that the viscosity increases upon RTFO-aging. Also note the relative distance between the original and RTFO curves for all four materials. The guayule-based materials have a wider separation than the petroleum-based binders which one would expect based upon the radical differences between the guayule-based materials and petroleum-based binders in terms of mass change upon RTFO-aging.

3.1.2.8 Summary of Task 2, part 1: material characterization. A summary of the results for this section is given in the following bullet-point list:

- Of the eleven different combinations of guayule feedstock material, solvent(s), and extraction/recovery processes investigated, LF and RR were selected for further, in-depth evaluations.
- Yields of the LF and RR were significant and were a factor in the decision to investigate these two extracts further.

- Binder contents of the RAPs and RAS, necessary for FPM design, were determined.
- Gradations of the RAPs and RAS, also necessary for FPM design, were determined.
- RA classification showed that the LF and RR exceeded mass change limits.
- The LF extract demonstrated counter-intuitive, but interesting behavior by becoming less viscous upon RTFO-aging.
- GC-MS testing indicated that the extract recovery process (desolventization) resulted in very effective removal of the acetone and hexane solvents.
- Viscosity testing of the original and RTFO-aged RAPs, RAS, and PG binders was performed with no unexpected results.
- Viscosity testing of the original and RTFO-aged LF, RR, and CycL was performed. These results, along with the PG binder viscosity results, were used for comparison purposes. The viscosity behavior of the LF was close to that of the PG52-28, and the RR behavior was similar to the CycL. Results of the comparisons were the major factor in deciding to compare the LF to the PG52-28, and the RR to the CycL.

3.1.3. Binder-Blending Mixture Experiment: Task 2, Part 2. In order to determine the relative effects of the guayule-based materials vs. the petroleum-based binders when blended with RAP/RAS binders, and to develop response surface models (RSMs) required for FPM design, binder-blending mixture experiments were developed. The experimental design matrices for the comparison of the LF and PG52-28 binders are given in Tables 3.8 and 3.9, and the matrices for the comparison of the RR and CycL binders are given in Tables 3.10 and 3.11. The “design” blend proportions were generated using the Design-Expert® software program based on constraints imposed on the proportion limits of each individual component. The proportion limits were based on the literature, practical considerations, and creating as much “data space” as possible for modeling purposes.

For the LF vs. PG52-28 and the RR vs. CycL binder-blending mixture experiments, the RAP1 and RAP2 design proportion limits were chosen to be 0 – 100%. This means that RAP1 and/or RAP2 could comprise up to 100% of the binder. As discussed in the literature review, there are FPM production facilities (i.e. asphalt plants) that can handle 100% reclaimed material.

The LF vs. PG52-28 mixture experiment was performed first because the LF material became available much earlier than the RR. For this analysis, the RAS design limits were set at 0 – 50% because some investigations into the use of RAS had looked at percentages (weight of processed RAS as a percentage of total mix weight) as high as 50% [91]. The RA design limits for this analysis were set at 0 – 70% based on knowing that the LF and PG52-28 were fairly viscous and high contents could be required to temper the very stiff RAP/RAS binders.

The RAS design limits were set at 0 – 15%, however, for the RR vs. CycL mixture experiment. The reduction of the RAS upper limit to 15% for the RR vs. CycL blends was a result of difficulties during testing of the some of the very stiff, high-RAS-content blends created in the LF vs. PG52-28 mixture experiment, which, again, occurred before the RR vs. CycL experiment; i.e. the experimentation was on a learning curve. Because the RR and CycL were much less viscous than the LF or PG52-28, and the supply of RR was limited, the upper design limit for the RR and CycL RAs was lowered to 30%.

Each blend (row) was physically created using a modified Brookfield rotational viscometer as a mixing device. Figure 3.10 shows the modified Brookfield viscometer setup for mixing the blends. Details about the blending procedure are in Appendix D.

Each blend was then tested to determine 1) the T_cH (high critical temperature) using a Dynamic Shear Rheometer (DSR), and 2) the T_cL (low critical temperature) using a Bending Beam Rheometer (BBR). An explanation of the T_cH and T_cL is given, below. Figure 3.11 shows the Rolling Thin Film Oven (RTFO), Pressure Aging Vessel (PAV), DSR, and BBR stations.

Figure 3.10. Modified Brookfield Viscometer for Binder Blending

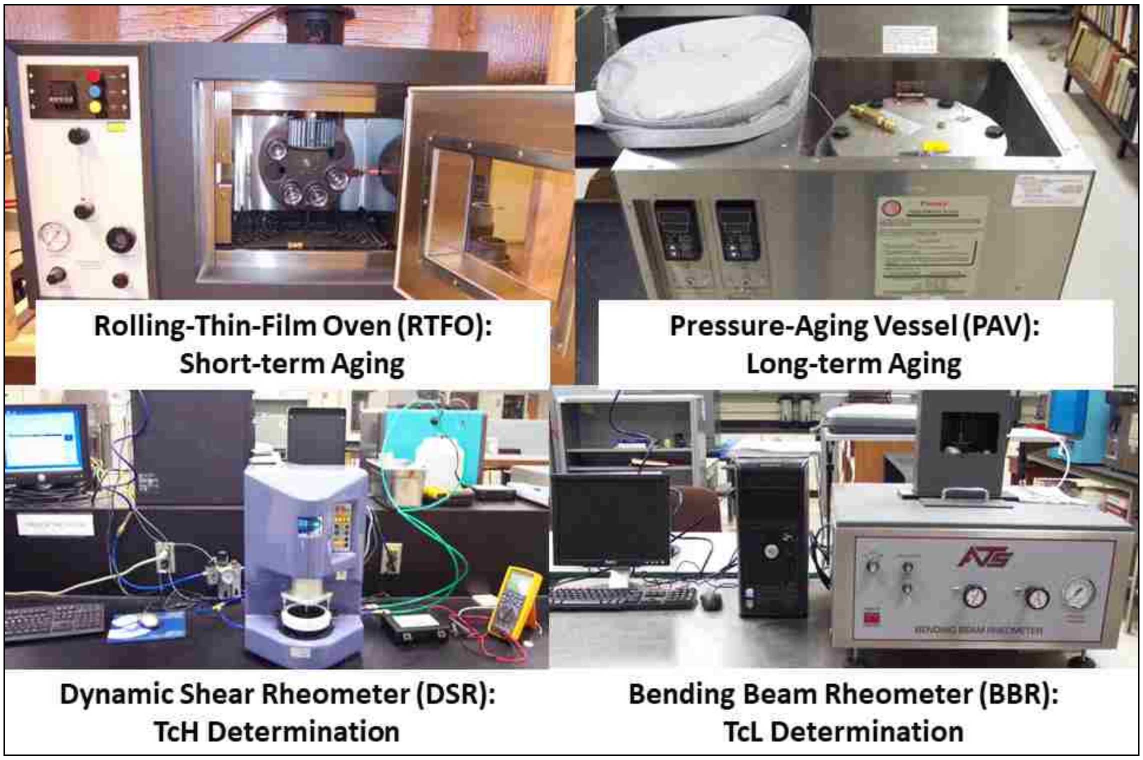


Figure 3.11. RTFO, PAV, DSR, and BBR Stations

Regarding the information given in Table 3.7, the high and low critical temperatures (T_cH and T_cL, respectively) are part of the basis for the grading of a PG binder under specifications set forth in AASHTO M 320 [92]. M 320 is still the predominant petroleum-based binder performance specification utilized by state DOTs.

The mixture experiment is a special type of methodology for generating response surface models (RSMs) for design. RSMs are, essentially, regression models with more than one independent variable. What sets the mixture experiment apart from other RSM designs is the fact that the level of each component (factor) is dependent on the levels of the other components; i.e. the percentages of each component must add up to 100%.

Table 3.7. High (T_cH) and Low (T_cL) Critical Temperature Determinations

Tests	Responses: Definitions and Criteria
Dynamic Shear Rheometer (DSR) testing of original binder (condition #1) and RTFO-aged binder (condition #2) [93] [94] [95]	T_cH = High critical temperature: An indicator of FPM rutting potential and the lowest (coolest), most conservative of the two temperatures determined under the following conditions: 1. The temperature at which the ratio of the complex modulus (G*) to the sine of the phase angle (sinδ) equals 1.00 kPa, as determined during DSR testing at 10 radians/second on ***original binder*.** 2. The temperature at which the ratio of the complex modulus (G*) to the sine of the phase angle (sinδ) equals 2.20 kPa, as determined during DSR testing at 10 radians/second on ***RTFO-aged binder*.**
Bending Beam Rheometer (BBR) testing of PAV-aged binder [94] [95] [96]	T_cL = Low critical temperature: An indicator of FPM cold-temperature (thermal) cracking potential and the highest (warmest), most conservative of the two temperatures determined under the following conditions: 1. The temperature at which the creep stiffness (S) equals 300 MPa at 60 seconds of loading. 2. The temperature at which the m-value (the absolute value of the slope of the logarithm of the stiffness curves versus the logarithm of the time) equals 0.300 at 60 seconds of loading.

Generation of the RSMs required ten experimental runs (i.e. data points or blends) in order to fit a Scheffe quadratic model to the data. Additionally, at least three additional unique blends were created to check for lack of fit, and at least four replicated tests (duplicates of some of the other blends) were generated to calculate pure error.

An example of “replicated tests” and “repeated measurements” is shown by looking at the 7th and 8th rows from the top of the data in Table 3.8 (50% RAP1 and 50% RAP2). Each of these batches of blended RAP was created separately using the modified Brookfield viscometer, described earlier, making them replicate blends. The T_cH and T_cL values for each replicate blend are the average of two test results or “repeated measurements,” i.e. tests performed on specimens sampled from the same batch. Since each replicate blend was created and tested in the same manner, all process variability was present making the 7th and 8th rows replicated tests.

Listed below each component in Tables 3.8 through 3.11 are the decimal percentage proportions (by weight) of each component per blend or run, and the colored blends indicate replicate tests where each pair of replicate tests is the same color.

Table 3.8. Binder-Blending Mixture Experiment: LF as Recycling Agent

Data Type	Blended-Binder Components/Proportions				Responses	
	RAP1	RAP2	RAS	LF	TcH (°C)	TcL (°C)
No-RA (shared) Data (Decimal % Proportions)	1.000	0.000	0.000	0.000	86.9	-8.3
	1.000	0.000	0.000	0.000	87.0	-8.1
	0.000	1.000	0.000	0.000	95.4	-0.9
	0.000	1.000	0.000	0.000	95.2	-1.0
	0.000	0.500	0.500	0.000	127.7	10.5
	0.000	0.500	0.500	0.000	127.3	10.6
	0.500	0.500	0.000	0.000	91.7	-4.4
	0.500	0.500	0.000	0.000	91.9	-4.2
	0.500	0.000	0.500	0.000	122.4	6.5
	0.750	0.000	0.250	0.000	102.1	-1.9
RA-Specific Data (Decimal % Proportions)	0.000	0.300	0.000	0.700	55.5	-14.5
	0.150	0.000	0.150	0.700	54.1	-16.5
	0.650	0.000	0.000	0.350	71.5	-9.0
	0.000	0.000	0.500	0.500	90.3	-4.8
	0.000	0.360	0.260	0.380	93.7	-1.6
	0.325	0.325	0.000	0.350	74.2	-6.2
	0.167	0.167	0.500	0.167	121.4	4.8
	0.000	0.650	0.000	0.350	78.4	-6.3
	0.360	0.000	0.260	0.380	88.5	-1.8

Two regression analyses were performed for each of the four tables: one to generate a T_cH RSM and another to generate a T_cL RSM. The component (RAP1, etc.)

percentages (in decimal form) were the independent variables, and the responses (T_cH and T_cL) were the dependent variables. In other words, T_cH and T_cL can be predicted from the proportions of the four binder materials: RAP1, RAP2, RAS, and the RA. To clarify the previous statement, Equations 1 and 2 are given below. They are the T_cH and T_cL RSMs (predictive equations) generated based on the RAP/RAS/RR data in Table 3.10. Equations 1 and 2 will be discussed in more detail in Section 3.1.5.

$$\begin{aligned} TcH = {} & 87.62(RAP1) + 94.33(RAP2) + 143.6(RAS) + 13.12(RR) + 4.678(RAP1 \times RAP2) \\ & - 45.59(RAP1 \times RR) - 55.90(RAP2 \times RR) - 118.0(RAS \times RR) \end{aligned} \tag{1}$$

$$\begin{aligned} TcL = {} & -6.309(RAP1) - 1.409(RAP2) + 27.03(RAS) - 1.979(RR) - 25.93(RAP1 \times RAS) \\ & - 83.28(RAP1 \times RR) - 109.0(RAP2 \times RR) - 152.2(RAS \times RR) \end{aligned} \tag{2}$$

It should be noted that for both comparisons (LF vs. PG52-28, and RR vs. CycL), the blends that do not include RA (i.e. No-RA or reclaimed binders only) were only created and tested once; i.e. that data was “shared” between the guayule-based RA and petroleum-based RA analyses.

Once the RSMs are established, DesignExpert can be used to “optimize” the component proportions to meet a desired T_cH and/or T_cL value or range of values. In other words, DesignExpert will try many combinations of proportions rapidly to arrive at the best (or several acceptable) combinations, rather than calculate it all manually. If possible, many different optimization solutions can be generated by DesignExpert imparting more flexibility in the FPM design process.

The term "original binder," as it is used in Table 3.7 when describing T_cH determination, means that the reclaimed RAP/RAS binder or blend, or a RAP/RAS/RA blend has not been subjected to any aging (i.e. RTFO or PAV) in the laboratory. In reality, however, the reclaimed binders have already experienced significant aging as a result of their in-service history. With this in mind, it is important to point out that none of the blends shown in Tables 3.8 – 3.11 were PAV-aged, although this is required for standard BBR testing, as described earlier. The blends were not PAV-aged because approximately half of the blends per table were entirely reclaimed binder(s), no RA. The AASHTO 323 Appendix [95] specifies that when characterizing reclaimed binders, RTFO-aging is sufficient and is used in-lieu of PAV-aging. Thus to keep from injecting another variable into the mixture experimental designs, all blends, those that had a RA and those that did not (i.e. No- RA), were RTFO-aged only when aging was required for testing. Therefore, the TcL RSMs generated are based on RTFO-aged binder which means that estimated T_cL values using the RSMs would be lower (cooler) than actual T_cL values based on PAV-aged binder.

Finally, any blend ultimately used in FPM design should first be verified as to whether or not it meets the required specifications using the appropriate test procedures, which would, normally, include testing of the PAV-aged blend. Therefore, although the testing and response descriptions given below in Table 3.12 are about verification testing, including T_cInt determination of PAV-aged binder, these descriptions are just definitions within the standard specifications. However, as discussed in the previous paragraph, no PAV-aging was performed on any of the blends in the binder-blending mixture experiments.

Table 3.9. Binder-Blending Mixture Experiment: PG52-28 as Recycling Agent

Data Type	Blended-Binder Components/Proportions				Responses	
	RAP1	RAP2	RAS	PG52-28	TcH (°C)	TcL (°C)
No-RA (shared) Data (Decimal % Proportions)	1.000	0.000	0.000	0.000	86.9	-8.3
	1.000	0.000	0.000	0.000	87.0	-8.1
	0.000	1.000	0.000	0.000	95.4	-0.9
	0.000	1.000	0.000	0.000	95.2	-1.0
	0.000	0.500	0.500	0.000	127.7	10.5
	0.000	0.500	0.500	0.000	127.3	10.6
	0.500	0.500	0.000	0.000	91.7	-4.4
	0.500	0.500	0.000	0.000	91.9	-4.2
	0.500	0.000	0.500	0.000	122.4	6.5
	0.750	0.000	0.250	0.000	102.1	-1.9
RA-Specific Data (Decimal % Proportions)	0.000	0.300	0.000	0.700	69.1	-19.3
	0.150	0.000	0.150	0.700	73.9	-18.3
	0.650	0.000	0.000	0.350	76.5	-14.6
	0.000	0.000	0.500	0.500	103.3	-4.7
	0.000	0.360	0.260	0.380	94.6	-5.3
	0.325	0.325	0.000	0.350	79.8	-12.4
	0.167	0.167	0.500	0.167	117.3	4.3
	0.000	0.650	0.000	0.350	83.4	-9.6
	0.360	0.000	0.260	0.380	91.0	-9.2

The MSCR test responses, $J_{nr(3.2)}$, $J_{nr(diff)}$, $R_{(3.2)}$, and $R_{(diff)}$ are determined through DSR testing as described in the AASHTO provisional test method TP 70 [97]. These responses are indicators of rutting potential, stress sensitivity, the presence of a polymer and, if present, the quality of blending of that polymer. The MSCR test is specified to be performed on RTFO-aged binder and the test temperature depends on the environmental high pavement temperature and is usually selected by the specifying agency. For example, MoDOT now allows the use of the AASHTO specification MP 19 [98] as a supplement to AASHTO M 320 [92], which is the PG binder specification MoDOT still uses in its contracts. If used, MoDOT specifies that the MSCR test be performed at 64°C on FPM binders used on Missouri state highways.

Table 3.10. Binder-Blending Mixture Experiment: RR as Recycling Agent

Data Type	Blended-Binder Components/Proportions				Responses	
	RAP1	RAP2	RAS	RR	TcH (°C)	TcL (°C)
No-RA (shared) Data (Decimal % Proportions)	1.000	0.000	0.000	0.000	87.7	-6.2
	1.000	0.000	0.000	0.000	87.5	-6.3
	0.000	1.000	0.000	0.000	93.9	-1.0
	0.000	1.000	0.000	0.000	94.5	-1.3
	0.210	0.718	0.072	0.000	97.1	-1.1
	0.210	0.718	0.072	0.000	97.0	-1.5
	0.648	0.202	0.150	0.000	97.8	-2.6
	0.832	0.162	0.006	0.000	90.1	-5.4
RA-Specific Data (Decimal % Proportions)	0.000	0.768	0.150	0.082	91.0	-5.8
	0.425	0.454	0.003	0.119	77.7	-13.0
	0.425	0.454	0.003	0.119	77.5	-14.4
	0.215	0.513	0.150	0.122	83.7	-10.4
	0.740	0.000	0.092	0.168	72.4	-17.0
	0.740	0.000	0.092	0.168	72.6	-17.4
	0.000	0.685	0.043	0.272	62.4	-22.5
	0.631	0.069	0.000	0.300	56.3	-22.5
	0.401	0.149	0.150	0.300	62.0	-22.4
	0.204	0.346	0.150	0.300	62.2	-22.6

In MP 19, traffic loading is the only other criteria for grading a binder when using the MSCR test. Traffic loading designations are "S" for standard, "H" for heavy, "V" for very heavy, and "E" for extremely heavy traffic. This traffic loading designation system replaces the "grade bumping" practice traditionally performed when following M 320.

Under MP 19, $J_{nr(3.2)}$ and $J_{nr(diff)}$ are the only criteria required for making pass/fail determinations.

For all temperatures and traffic loading designations, $J_{nr(diff)}$ cannot exceed 75%. The maximum $J_{nr(3.2)}$ value, on the other hand, is a function of traffic but not temperature. For example, $J_{nr(3.2)}$ cannot exceed 4.0 kPa^{-1} for the standard traffic "S" grade but the maximum $J_{nr(3.2)}$ is lowered to 1.0 kPa^{-1} for the very heavy traffic "V" grade. $R_{(3.2)}$ and $R_{(diff)}$ are obtained through MSCR testing and are used to determine the elastic response and stress dependence of polymer modified and neat binders, but they are not required as part of MP 19.

Table 3.11. Binder-Blending Mixture Experiment: CycL as Recycling Agent

Data Type	Blended-Binder Components/Proportions				Responses	
	RAP1	RAP2	RAS	CycL	TcH (°C)	TcL (°C)
No-RA (shared) Data (Decimal % Proportions)	1.000	0.000	0.000	0.000	87.7	-6.2
	1.000	0.000	0.000	0.000	87.5	-6.3
	0.000	1.000	0.000	0.000	93.9	-1.0
	0.000	1.000	0.000	0.000	94.5	-1.3
	0.210	0.718	0.072	0.000	97.1	-1.1
	0.210	0.718	0.072	0.000	97.0	-1.5
	0.648	0.202	0.150	0.000	97.8	-2.6
	0.832	0.162	0.006	0.000	90.1	-5.4
RA-Specific Data (Decimal % Proportions)	0.000	0.768	0.150	0.082	91.3	-6.4
	0.425	0.454	0.003	0.119	76.1	-14.4
	0.425	0.454	0.003	0.119	76.3	-15.2
	0.215	0.513	0.150	0.122	84.0	-11.7
	0.740	0.000	0.092	0.168	72.0	-19.1
	0.740	0.000	0.092	0.168	72.2	-19.6
	0.000	0.685	0.043	0.272	62.7	-23.5
	0.631	0.069	0.000	0.300	54.9	-23.7
	0.401	0.149	0.150	0.300	61.0	-23.8
	0.204	0.346	0.150	0.300	62.1	-23.9

Table 3.12. Binder Blend Verification Tests

AASHTO M 320 Tests	Responses: Definitions and Criteria
Dynamic Shear Rheometer (DSR) testing of original binder (condition #1) and RTFO-aged binder (condition #2) [93] [94] [95]	T_cH = High critical temperature: An indicator of FPM rutting potential and the lowest (coolest), most conservative of the two temperatures determined under the following conditions: 1. The temperature at which the ratio of the complex modulus (G^*) to the sine of the phase angle ($\sin\delta$) equals 1.00 kPa, as determined during DSR testing at 10 radians/second on ***original binder.*** 2. The temperature at which the ratio of the complex modulus (G^*) to the sine of the phase angle ($\sin\delta$) equals 2.20 kPa, as determined during DSR testing at 10 radians/second on ***RTFO-aged binder.***
Bending Beam Rheometer (BBR) testing of PAV-aged binder [94] [95] [96]	T_cL = Low critical temperature: An indicator of FPM cold-temperature (thermal) cracking potential and the highest (warmest), most conservative of the two temperatures determined under the following conditions: 1. The temperature at which the creep stiffness (S) equals 300 MPa at 60 seconds of loading. 2. The temperature at which the m-value (the absolute value of the slope of the logarithm of the stiffness curves versus the logarithm of the time) equals 0.300 at 60 seconds of loading.
Dynamic Shear Rheometer (DSR) testing on PAV-aged binder [93] [94] [95]	T_cInt = Intermediate critical temperature: An indicator of FPM fatigue cracking potential and the temperature at which the product of G^* and $\sin\delta$ equals 5000 kPa as determined during DSR testing at 10 radians/second.
Brookfield Rotational Viscometer testing [87] [92]	Maximum viscosity at 135°C = 3 Pa·sec = 3000 centipoise
Flash Point testing [88] [92]	Minimum flash point = 230°C
Mass Change testing [85] [92]	Maximum mass change = ±1.00%
AASHTO MP 19 Tests	Responses: Definitions and Criteria
Multiple Stress Creep Recovery (MSCR) testing on RTFO-aged binder using a DSR: All averages based on 10 creep – recovery cycles [97] [98]	1. $J_{nr(3.2)}$ [$J_{nr(0.1)}$] = Average non-recoverable creep compliance at 3.2 kPa of creep stress [and 0.1 kPa, respectively] 2. $J_{nr(diff)}$ = Percent difference between $J_{nr(0.1)}$ and $J_{nr(3.2)}$ 3. $R_{(3.2)}$ [$R_{(0.1)}$] = Average percent recovery at 3.2 kPa of creep stress [and 0.1 kPa, respectively] 4. $R_{(diff)}$ = Percent difference between $R_{(0.1)}$ and $R_{(3.2)}$

In this study, the MSCR test was originally intended to be run just after each T_cH determination, thereby generating several more data responses per blend to use in any subsequent analyses. However, the DSR software would occasionally crash during the last few cycles of the MSCR test. Therefore, the MSCR data collected during the binder-blending mixture experiment is incomplete. But as will be discussed later, the MSCR test was successfully used to verify the chosen blend for mix design, production, and testing.

A summary of results for this section is given in the following bullet-point list:

- DesignExpert software was used to generate design proportions for blends of the RAPs, RAS, and RAs based on selected limits of each component.
- For each of the four RAs used in this comparative analysis (LF vs. PG52-28, and RR vs. CycL), blends were created based on the design proportions. 56 different blends were created using a modified Brookfield viscometer.
- T_cH and T_cL were determined for all 56 batched blends. All T_cH and T_cL reported values were the average of two repeated measurements.

3.1.4. LF vs. PG52-28 and RR vs. Cyclogen L Comparisons. The RA-specific data in Tables 3.8 –3.11 (i.e. those blends that include a RA) was used to develop Figures 3.12 – 3.17. These plots show the correlations between the T_cH and T_cL, and the absolute temperature spread ($T_cH – T_cL$) of the materials being compared. A wider absolute temperature spread means better overall performance.

As indicated in Figures 3.12 – 3.14, the PG52-28-RAP/RAS blends generally had higher (warmer) T_cH values, lower (cooler) T_cL values, and, therefore, generally larger absolute temperature spreads than the proportionally-identical LF-RAP/RAS blends.

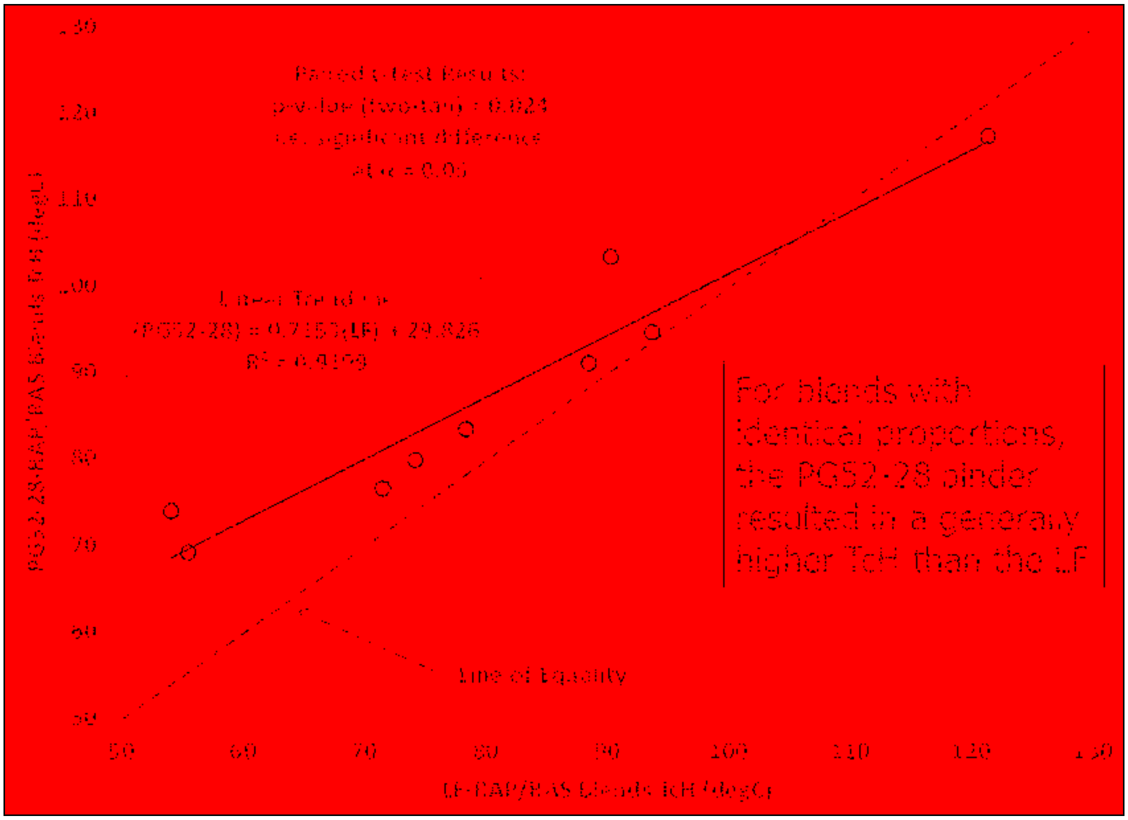


Figure 3.12. T_cH Correlation (LF vs. PG52-28)

The results presented in Figures 3.12 – 3.14 were discouraging. Though the LF did not favorably compare in a direct manner to the PG52-28 binder, the LF material, because of its guayule rubber (GR) content, may prove useful as a polymer-modifier to increase the high-temperature performance of a FPM while holding the low-temperature performance constant. This speculation applies to any resin that might contain some GR, low MW and/or high MW. Nonetheless, the results presented in this section focused the remaining effort in the NCHRP-IDEA project on the RR. Figures 3.15 – 3.17 show the same correlations for the RR vs. CycL comparison.

The plots in Figures 3.15 – 3.17 clearly show that the RR vs. CycL direct comparisons are much more favorable than the LF vs. PG52-28. The T_cH correlation is almost perfect but slightly favors the RR. The T_cL correlation definitely favors the CycL but the bias is only a degree or two on average. The absolute temperature spread correlation is significantly different at an alpha value of 0.05, but, again, is only slightly biased toward the CycL, and not for every blend. These results demonstrated that the RR could be used in a practical sense as a RA, and prompted the move to start FPM design, production, and testing.

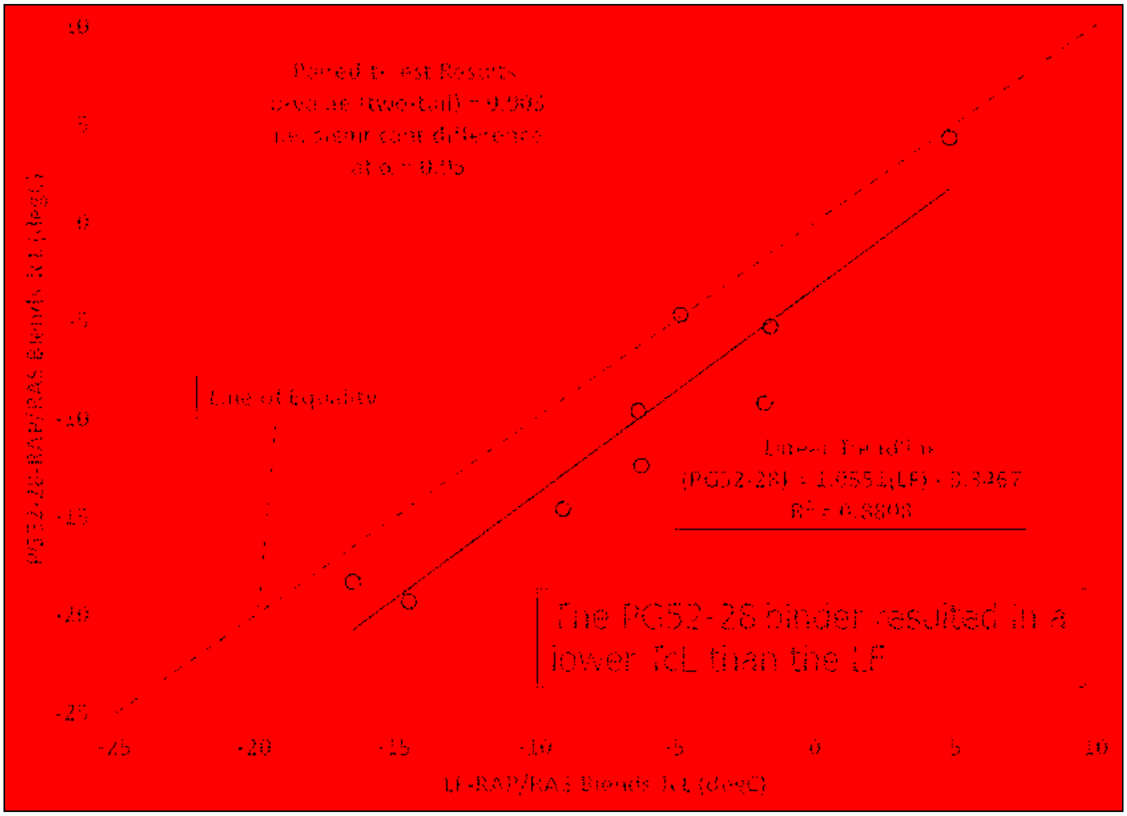


Figure 3.13. T_cL Correlation (LF vs. PG52-28)

A summary of results for this section is given in the following bullet-point list:

- Simple correlations of the T_cH, T_cL, and $T_cH – T_cL$ parameters were performed for each pair of RAs analyzed on a comparative basis: LF vs. PG52-28, and RR vs. CycL.

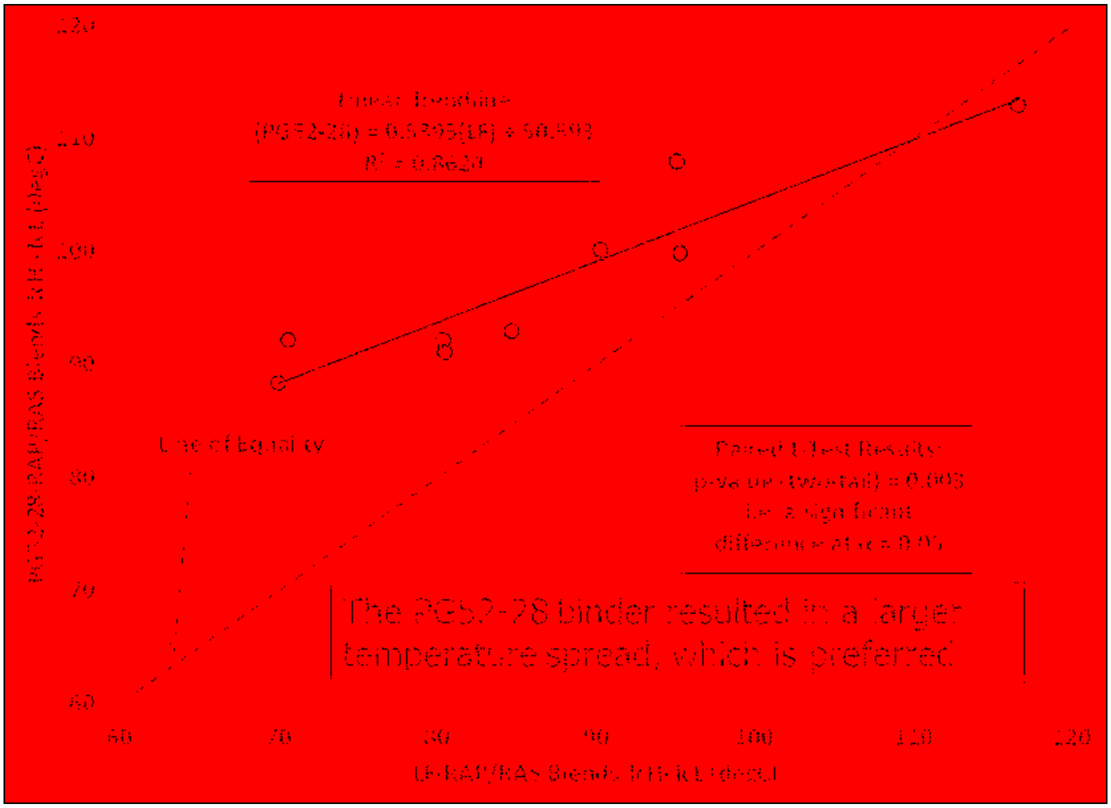


Figure 3.14. $T_cH – T_cL$ Correlation (LF vs. PG52-28)

- Based on the simple correlations, the LF extract was discontinued as a subject of further evaluation as a RA. TcH – TcL of the LF blends, compared to the PG52-28 blends, was smaller by ~10°C, on average, and more variable; i.e.

standard deviation of TcH – TcL for the LF blends was 14.5°C versus 8.4°C for the PG52-28 blends. However, because the LF contained some rubber, it may prove useful as a polymer-modifier to increase the high-temperature performance of a FPM while holding the low-temperature performance constant.

- The RR vs. CycL correlations showed that the RR could, in a practical sense, serve as a RA. Therefore, RR became the focus of the remainder of the study.

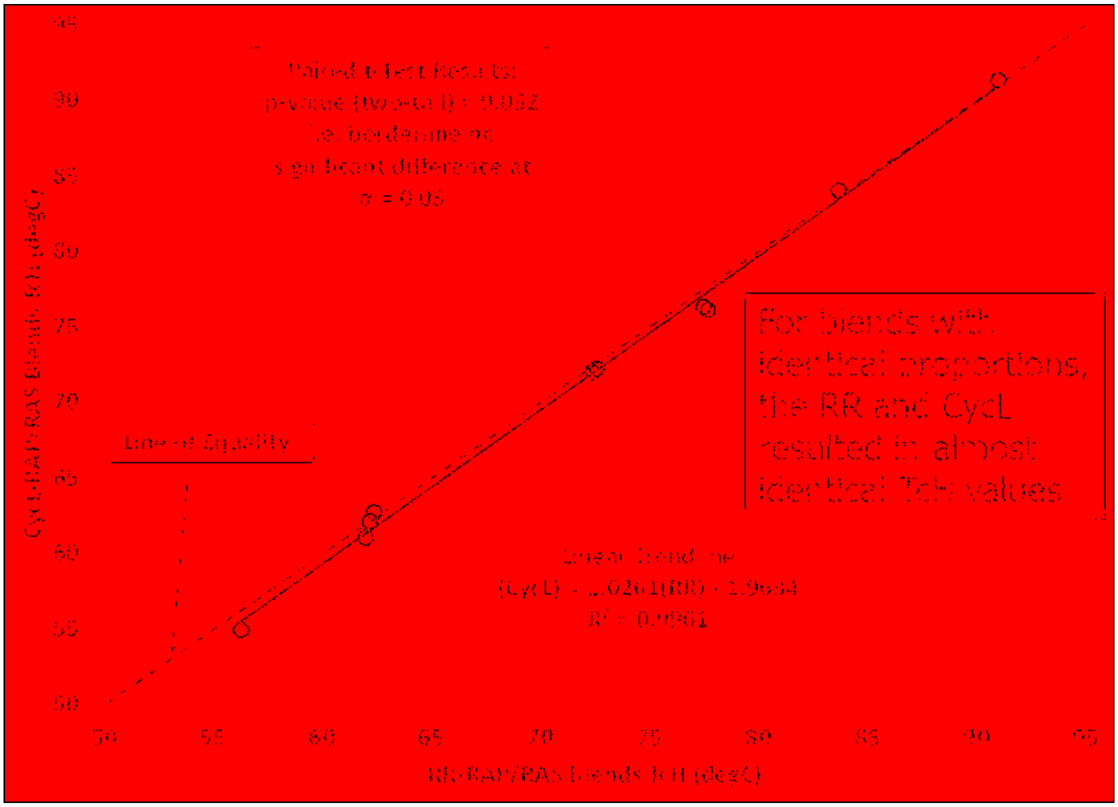


Figure 3.15. T_cH Correlation (RR vs. CycL)

3.1.5. Response Surface Models: Generation and Optimization. Generation of the response surface models (RSMs) was performed using regression analysis procedures within DesignExpert using the data in Tables 3.8 – 3.11. It is important to reiterate, two RSMs were generated per table: one for T_cH and one for T_cL. As the focus was now only on the RR, only the RR RSMs were necessary to utilize and are repeated, below, in Equations 1 and 2, where the independent variables (RAP1, etc.) are the decimal fractions of the proportions in a given blend.

$$\begin{aligned} TcH = {} & 87.62(RAP1) + 94.33(RAP2) + 143.6(RAS) + 13.12(RR) + 4.678(RAP1 \times RAP2) \\ & - 45.59(RAP1 \times RR) - 55.90(RAP2 \times RR) - 118.0(RAS \times RR) \end{aligned} \quad (1)$$

$$\begin{aligned} TcL = {} & -6.309(RAP1) - 1.409(RAP2) + 27.03(RAS) - 1.979(RR) - 25.93(RAP1 \times RAS) \\ & - 83.28(RAP1 \times RR) - 109.0(RAP2 \times RR) - 152.2(RAS \times RR) \end{aligned} \quad (2)$$

The goodness-of-fit statistics for Equations 1 and 2 are as follows:

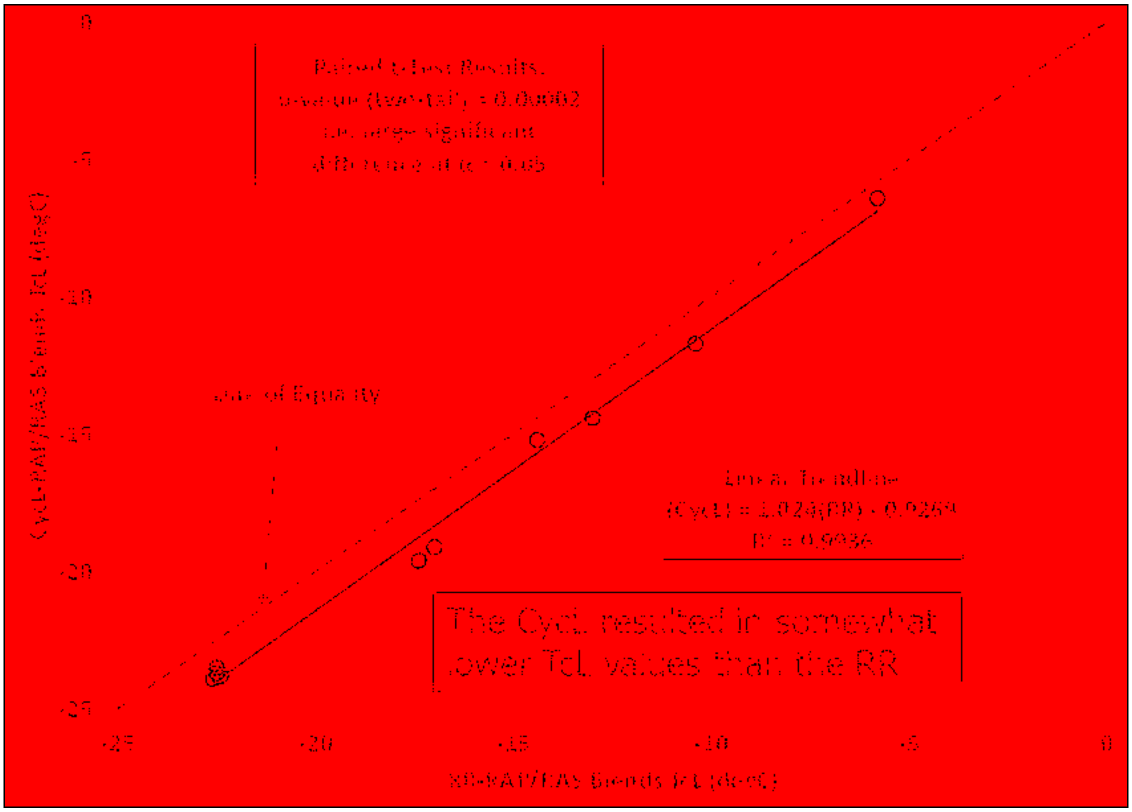
- Equation 1 (T_cH): Adjusted $R^2 = 0.9992$, Predicted $R^2 = 0.9888$.
- Equation 2 (T_cL): Adjusted $R^2 = 0.9974$, Predicted $R^2 = 0.9832$.

Before the beginning of the FPM design procedure, a particular blend had to be developed that would result in a desired grade of binder. The DesignExpert optimization process was utilized to determine sets of component proportions (or solutions) that would generate a blend meeting the specifications for a PG64-22 binder. The solutions were based on the RR T_cH and T_cL RSMs shown in Equations 1 and 2.

If one should choose to use Equations 1 and 2, the component proportions (independent variable values) should be in the form of decimal percentages, and the sum of those percentages must be 1.00 (i.e. 100%). For example, if one wanted to estimate

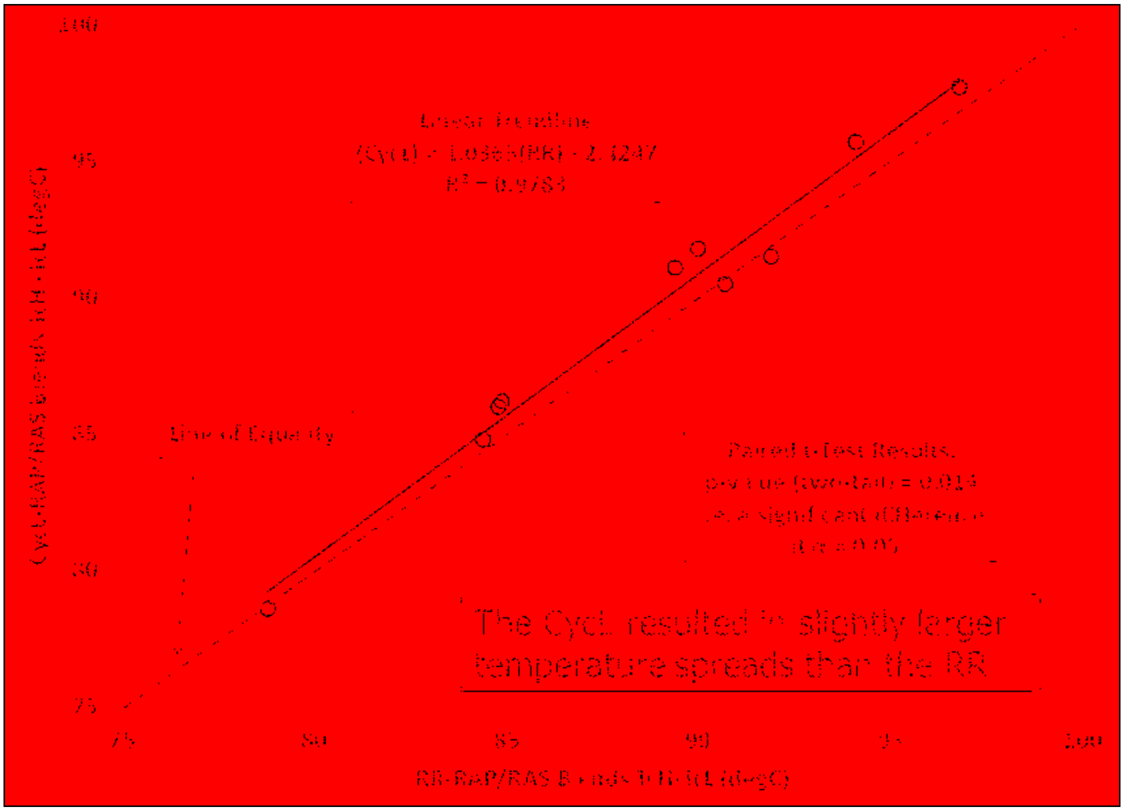
T_cH for a blend that had 70% RAP1, 0% RAP2, 5% RAS, and 25% RR (all percentages sum to 100%), one would input 0.70 everywhere RAP1 appears in Equation 1, 0.00 everywhere RAP2 appears in Equation 1, 0.05 everywhere RAS appears in Equation 1, and 0.25 everywhere RR appears in Equation 1. The same procedure would be used for estimating T_cL, Equation 2. It is very important to remember, however, that the regression coefficients on the main effects terms and the interaction terms are specific to the materials used in this project.

Figure 3.18 shows the DesignExpert optimization output for producing a blend estimated to meet specifications for a PG64-22 binder.



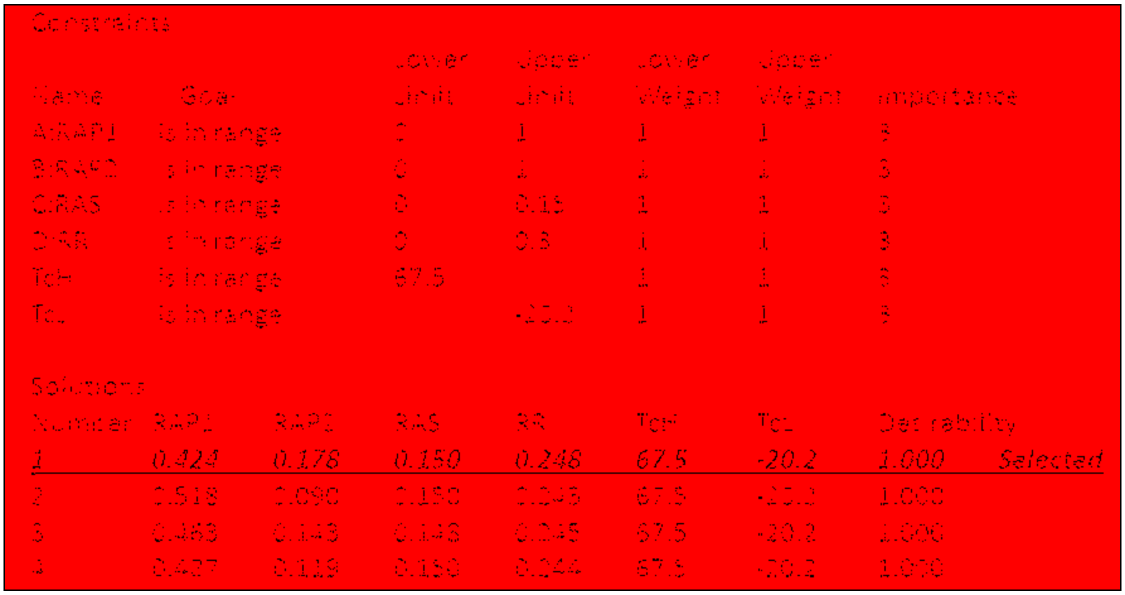
The CycL resulted in somewhat lower TcL values than the RR

Figure 3.16. T_cL Correlation (RR vs. CycL)



The CycL resulted in slightly larger temperature spreads than the RR

Figure 3.17. $T_cH – T_cL$ Correlation (RR vs. CycL)



Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:RAP1	is in range	0	1	1	1	3
B:RAP2	is in range	0	1	1	1	3
C:RAS	is in range	0	0.15	1	1	3
D:RR	is in range	0	0.3	1	1	3
TcH	is in range	67.5		1	1	3
TcL	is in range		-20.2	1	1	3

Solutions

Number	RAP1	RAP2	RAS	RR	TcH	TcL	Desirability	
1	*0.424*	*0.178*	*0.150*	*0.246*	*67.5*	*-20.2*	*1.000*	*Selected*
2	0.518	0.090	0.150	0.243	67.5	-20.2	1.000	
3	0.463	0.143	0.148	0.245	67.5	-20.2	1.000	
4	0.427	0.119	0.150	0.244	67.5	-20.2	1.000	

Figure 3.18. Optimization Solutions to Meet PG64-22 T_cH and T_cL Specifications

The optimization constraints (i.e. lower and upper limits) on the RAPs, RAS, and RR proportion limits shown in Figure 3.18 were selected to be the same as those used in the design proportion generation at the very beginning of the binder-blending mixture experiments. This selection utilizes the entire data space created during the testing of the various design blends. The “response” constraints shown in Figure 3.18 were chosen such that estimated T_cH would be greater than or equal to 67.5°C and the T_cL would be less than or equal to -20.2°C. The “weight” and “importance” of each constraint setting could also be adjusted, but were left at their default values for this project.

At this point, it is necessary to understand that there is a 10°C offset on the T_cL value when actually identifying a PG binder. During development of the standard BBR test procedure [96], a time/temperature superposition phenomenon was observed that was adopted in the test procedure. Researchers noticed that if the test temperature was increased 10°C (thereby decreasing the stiffness) and the loading time was decreased from two hours to 60 seconds, they obtained similar deflection results [99]. Therefore, in order for a binder to meet the specification for, say, a PG64-22 binder, the T_cH must be greater than or equal to 64°C (thus the estimated T_cH response constraint of 67.5°C, which allows for a 3.5°C margin of estimation error), and the T_cL must be less than or equal to -12°C. Remember that the T_cL is, by specification, to be determined on PAV-aged binder. Therefore, selection of -20.2°C as the upper threshold T_cL temperature for optimization purposes was based on engineering judgment knowing that the T_cL RSMs were based on RTFO-aged blends, which are not expected to be as stiff, generally speaking, as PAV-aged blends.

Solution #1 in Figure 3.18 is only one of four solutions found in the optimization process that has the highest possible desirability rating of 1.000. Solution #1 is bolded and italicized because it was selected as the beginning blend for FPM design. Based on discussion in the previous paragraph, the estimated "true" grade of the Solution #1 blend is PG67.5-30.2, again remembering that none of the mixture experiment blends were PAV-aged.

The next step was to physically build the Solution #1 blend, to be referred to as the RR5 blend (a blend made using RR from the 5th batch of 8 extraction batches), and verify that it did, indeed, meet the specifications for a PG64-22 binder.

Binder grade verification testing, as described in Table 3.12, was performed on the RR5 blend. Its true grade was determined to be PG65.5-24.3 even after appropriate PAV-aging of the blend per M 320 specifications.

MSCR testing was performed per TP-70 [97] and the RR5 blend met the PG64-22S (standard traffic) grade specifications set forth in MP-19 [98]. Rotational viscosity of the original (non-aged) RR5 blend at 135°C was 390 centipoise or 0.39 Pa·sec, well below the maximum limit of 3 Pa·sec.

Flash point was not determined. It was assumed that the RR5 blend would easily meet the minimum of 230°C based on the high RAP/RAS content and the fact that the RR pure blend (not-blended with other materials) flash point was 213°C.

The RR5 blend, however, did not meet the mass change specification. Mass change was -3.1% and the maximum allowable change is ±1.0%. The importance of meeting the mass change limits is debatable. The rationale behind its continued inclusion as a material specification in light of all of the new bio-based binder modifiers is not clear at this time.

FPM design was initiated knowing that the RR5 blend met nearly all of the specifications for a PG64-22 binder.

3.1.6. Flexible Pavement Mixture Design, Production, and Testing: Task 3. It is important to point out that for all of the design, production, and testing of FPMs, CycL was used in lieu of the RR during the initial trial runs because of the limited amount of RR on hand. For example, it was not until CycL-based FPM volumetric properties were close to the targets that FPMs using RR were produced and tested. This use of CycL for the initial trials did not mean, however, that the subsequent RR-based FPM volumetric properties met the targets upon the first few trial runs. Remember that the RR and CycL had similar, but not identical, viscosity-temperature relationships which meant that performing several trial runs using the RR was not unexpected.

3.1.6.1 FPM design and production. The goals of the FPM design process were to achieve a blend of reclaimed and virgin materials (aggregates and binder, and the RR) that would: 1) achieve the desired binder grade (e.g. PG64-22), 2) meet gradation specifications, and 3) meet state DOT FPM volumetric criteria (% air voids, % voids in the mineral aggregate or VMA, and % voids filled with asphalt or VFA). Using the verified RR5 blend discussed in Section 3.1.5, a spreadsheet was developed to control the blended-binder grade and the aggregate gradation of the FPM. The FPM design given in the spreadsheet was the first to be attempted in the laboratory and used no virgin petroleum-based binder. The FPM design spreadsheet and usage details are given in Appendix E.

Following specification-verification of the RR5 blend, all effort had been focused on producing a FPM that met, preferably, MoDOT Superpave specifications (i.e. SP125), or alternatively, plant mix bituminous pavement/base specifications (i.e. BP-1). However, many attempts to use the RR5 blend in a SP125 mix failed to produce a FPM meeting the volumetric and dust-to-effective binder ratio (D/P_{be}) specifications; there are just too many fines in the RAPs. It seemed that the only way to achieve a high-RAP/RAS FPM that meets Superpave specifications would be to fractionate the RAPs into two or more fractions thus allowing for much more gradation control. Of course, this would require much more characterization testing of the fractionated RAPs (FRAPs). Failure to produce a SP125 FPM using the RR5 blend and high percentages of RAP/RAS shifted the focus to producing a FPM using the RR5 blend that would meet BP-1 specifications.

MoDOT requires the use of a modified Marshall FPM design procedure for BP mixes but allows for the use of 150 mm diameter, gyratory-compacted specimens (GCSs) for volumetric determination, when applicable. Once a design gradation is determined, at least three total binder contents (at a maximum separation of 0.5%) are to be evaluated.

The original RR5 blend FPM design (given in Appendix E) was used as the starting point for subsequent FPM designs. The combined gradation met the BP-1 specification, and there was no virgin, petroleum-based binder (i.e. PG64-22) added to the mixture, a feature that was highly relevant to the original NCHRP-IDEA project concept. However, after many trial batches (again, using CycL in lieu of the RR during some of the initial trials), it became apparent that the original RR5 blend FPM design was not conducive to producing a BP-1 mix with no added virgin petroleum-based binder, and satisfying volumetric specifications.

Three total binder contents were evaluated per the Marshall mix design method. The low-level binder content was satisfied by the basic RR5 blend FPM design, but the mid-level and high-level total binder content FPMs had some PG64-22 added to the basic RR5 blend FPM. For each FPM design, sufficient mix was produced for a theoretical maximum specific gravity (G_{mm}) specimen and two, 150 mm diameter GCSs. All specimens were treated the same during production and each GCS was compacted using the MoDOT-specified 35 gyrations. The results are shown in Table 3.13.

Table 3.13. RR5 FPM Design Results

Property Binder Level	P_b (%)**	PG64-22 (%)**	P_{be} (%)**	D/P_{be}	GCS Height (mm)*	Air Voids (%)*	VMA (%)	VFA (%)
Low	4.28	0.00	3.64	2.03	117.8	5.83	14.2	58.7
Mid	4.58	0.31	3.94	1.87	116.2	4.60	13.7	66.4
High	4.88	0.63	4.25	1.74	114.8	3.47	13.4	74.1
BP-1 Spec.				***	110 – 120	3.5	≥13.5	60 – 80

* Based on the average of two specimens
**Based on mix weight
***No MoDOT specification (spec.); BP-1 mix designers strive for D/P_{be} of 1.5 – 2.0

As can be seen in Table 3.13, a P_b of 4.88% should result in a FPM with the desired level of air voids and VFA. However, VMA would be borderline out-of-specification, and VMA could be argued to be the most important volumetric property to use for prioritizing FPM design selection. Many designers purposely select designs with VMA levels 0.5% higher than the required minimum. This is especially true when there is RAP/RAS in the FPM because the use of the effective specific gravity (G_{se}) of the

RAP/RAS as a substitute for the RAP/RAS aggregate bulk specific gravity (G_{sb}) artificially inflates the calculated VMA of the FPM, and MoDOT requires the use of G_{se} in RAP/RAS FPM designs. Therefore, because the RAP/RAS content was so high for the RR5 FPM, 4.50% was chosen as the design P_b content as it should produce a VMA of about 13.8% and a VFA that is still within specification limits. However, it was expected that air void levels would be higher than desired but still within a generally acceptable level of 4 ± 1%.

Four batches of FPM were ultimately produced using the original no-virgin-binder design but with 30 grams of PG64-22 added (i.e. P_b of 4.50%). Prior to batching the aggregates, the RAPs were split (fractionated) on the ¼ inch screen in an effort to better control the gradation during batching. The percentages of the -¼ inch (percent passing the ¼ inch sieve or P1/4″) and +¼ inch (percent retained on the ¼ inch sieve or R1/4″) for each RAP were determined and, during batching of the RAPs, the P1/4″ and R1/4″ fractions were recombined at the same percentages. This was done to assure that the RAP binder properties were not changed; i.e. without knowing the binder content and grade of each FRAP, recombining them in proportions other than the original percentages could have affected the total reclaimed binder content and/or blended binder grade.

To minimize variability in the FPM batching process, each of the six aggregates (the four FRAPS, the RAS, and the ⅜ inch clean) were reduced through splitting such that each half of the last split was used to build one FPM batch; one half for a RR-based FPM and the other half for a CycL-based FPM. This process was repeated twice resulting in two aggregate batches, or four FPM batches. The CycL for both CycL batches came from the same 5-gallon can while the RR for each RR batch came from two previously extracted/recovered samples (i.e. batches RR-6 and RR-7; see Table 3.3). The design for this FPM with 30 grams of PG64-22 virgin binder is also included in Appendix E.

For each of the four FPM batches, sufficient mix was produced for a G_{mm} specimen and two, 150 mm diameter GCSs. All specimens were treated the same throughout the production process and all eight GCSs were compacted using 35 gyrations. The results are shown in Table 3.14.

Table 3.14. RR and CycL FPM Volumetric Comparison

Property	GCS Height (mm)		Air Voids (%)		VMA (%)		VFA (%)	
Recycling Agent	RR	CycL	RR	CycL	RR	CycL	RR	CycL
Batch1-GCS1	116.9	115.0	5.28	3.90				
Batch1-GCS2	116.4	115.2	4.99	4.08				
Batch1 Mean	116.7	115.1	5.13	3.99	14.2	13.4	63.9	70.1
Batch2-GCS1	114.1	114.5	3.29	3.53				
Batch2-GCS2	114.2	114.6	3.38	3.67				
Batch2 Mean	114.2	114.6	3.33	3.60	12.6	13.0	73.5	72.3
Overall Mean			4.24	3.80	13.4	13.2	68.7	71.2
BP-1 Specification	110 – 120		3.5		≥13.5		60 – 80	

The batch-to-batch variability of the RR FPMs is high and is speculated to be a function of differences between the RR-6 and RR-7samples used for FPM batching. Over an extended period of time, solids resembling fat globules would form in the RR and settle on the bottom of the storage container. The formation of these solids was probably due to oxidation of unsaturated fatty acid triglycerides [47] in the RR. The separation of the more viscous compounds from the RR was not accounted for before obtaining the RR from the container for mixing Batch2. The RR used for Batch2 was, apparently, the less viscous portion of the two separation phases in the storage container. It was placed into the mixing bucket and, not surprisingly, reduced the overall binder blend viscosity relative to Batch1. This reduced viscosity was reflected in reduced resistance to compaction and resulted in a relatively shorter specimen with a considerably lower VMA and % air voids.

Setting the variability issue aside, the basic FPM design resulted in a fair mix;

- % air voids were slightly high of specification, but fell in the generally acceptable range of 4 ± 1%.
- VMA was within 0.1% of meeting specification.
- VFA met specification.
- The FPM utilized 53% reclaimed aggregate (from the RAPs and RAS) which means major cost savings.
- Only 0.23% of the total FPM mass (or 5.62% of total binder mass) was virgin PG64-22 binder, a result that relates favorably to the IDEA project concept.
- The rest of the binding materials was reclaimed RAP/RAS binder (i.e. more cost savings) and RR as the RA.

3.1.6.2 Hamburg wheel-track testing. Hamburg wheel-track testing of the FPM was performed using the same FPM design reflected in Table 3.14 results except specimen mass and thickness was controlled to produce 150 mm diameter specimens with a % air voids of 7±1% as recommended in the T 324 procedure [100]. The batching procedure was the same as described in the previous section, and four GCSs were produced per RA. A Hamburg specimen was produced by cutting two, 62 mm thick

GCSs in such a manner that when butted against one another resulted in a continuous wheel path approximately 10 inches long. Two Hamburg specimens were submerged in 50°C water and subjected to 20,000 wheel passes, or however many passes that produced a pre-determined, maximum impression depth based on the applicable specification (the software default of 14 mm was used for this study). A full 20,000 wheel passes takes about 7 hours to complete. Figure 3.19 shows the Hamburg test results. Figure 3.20 shows the Hamburg wheel-track device.

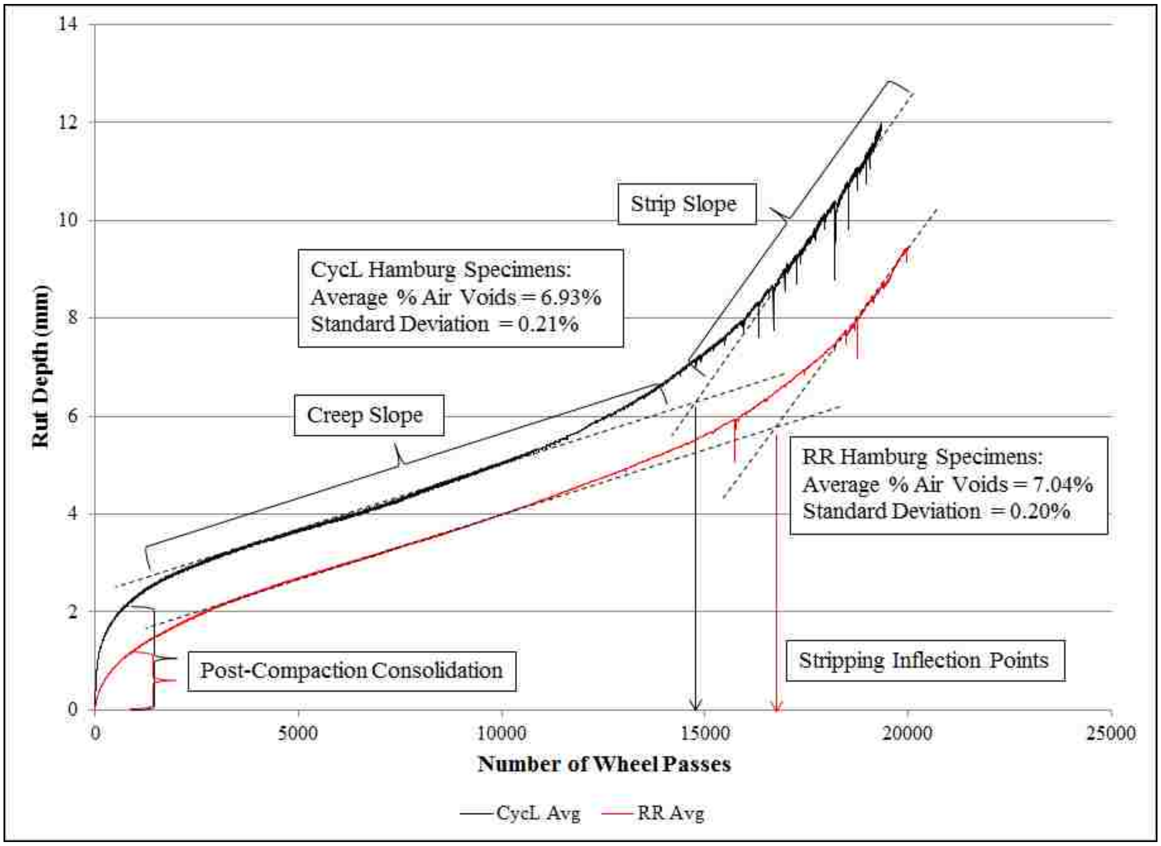


Figure 3.19. RR vs. CycL FPM-Hamburg Wheel-Track Testing Comparison

Hamburg wheel-track testing is a good indicator of rutting and stripping (moisture damage) potential of a FPM. There are four basic parameters identified in Figure 3.19: post-compaction consolidation, creep slope, strip slope, and stripping inflection point. Post-compaction consolidation is usually taken at 1000 wheel passes and is considered to be the result of the wheel load densifying the mixture. Creep slope is a measure of the rutting susceptibility due to gradation, binder stiffness, particle shape, etc., but not moisture damage. The stripping inflection point and strip slope are measures of moisture damage. Where the strip slope is a measure of accumulated deformation due to moisture damage, the stripping inflection point is a way to identify when the mixture performance becomes mostly a function of moisture damage. The Colorado Department of Transportation reports that a stripping inflection point occurring before 10,000 wheel passes indicates a stripping susceptible FPM [101].

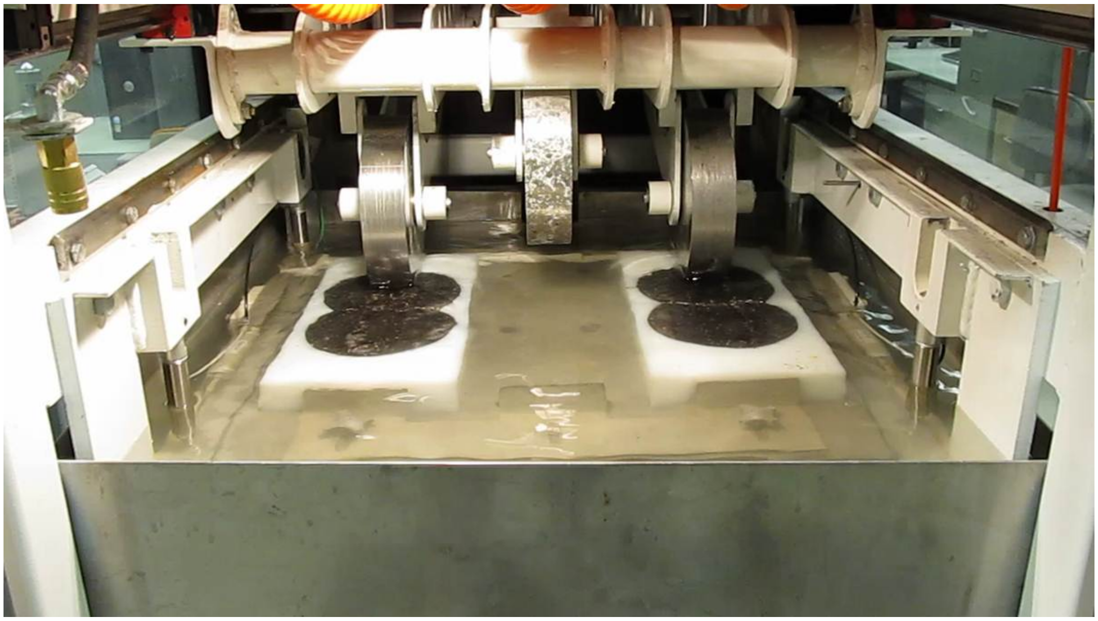


Figure 3.20. Hamburg Wheel-Track Test

The test data from two Hamburg specimens was averaged to produce the curves shown in Figure 3.19. The test method recommends a void content of 7 ± 1% for the test specimens. The average voids content (based on four GCSs) for each mix is indicated on Figure 3.19 and shows that the voids in the CycL specimens compare very closely with the RR specimens having slightly higher voids. Variability among the GCSs voids content is essentially the same for each mix.

In making conclusions about the results shown in Figure 3.19, one must consider that the short-term aged viscosity of the RR is slightly higher than the short-term aged viscosity of the CycL. The increased post-compaction consolidation of the CycL FPM relative to the RR FPM could be due to this viscosity differential. All other major properties of the two FPMs (aggregate gradation, particle shape and geology, binder content, and volumetrics) are, however, essentially the same. The creep and strip slopes of both FPMs are parallel indicating that the rates of deformation due to non-moisture and moisture-induced damage are identical. However, the locations of the stripping inflection points indicate that the RR FPM performed better than the CycL FPM insofar as the onset of moisture damage is concerned. Because of the slight short-term aged viscosity differential between the RR and the CycL, one can conservatively conclude that the RR FPM performed as well as the CycL FPM in the Hamburg tests. Work is underway on precision statements for this test method.

3.1.6.3 Tensile strength ratio (TSR) testing. The Tensile Strength Ratio (TSR) test, arguably the most widely used standard test for evaluating the stripping potential of FPMs, was performed on RR and CycL FPMs, again, for comparative purposes [102]. The same process and FPM design used to produce the Hamburg GCSs was used for producing the TSR specimens. Six, 95 mm thick, 150 mm diameter GCSs per RA were produced with a specified % air voids of 7 ± 0.5% as the target.

After determining the actual % air voids for each GCS, the six were grouped into two groups of three specimens each such that the average % air voids of each group was approximately equal. One group of three specimens was designated as the unconditioned (dry) set and the other group of three specimens was designated as the conditioned (wet). Conditioning of the wet set and handling of the dry set of specimens were performed per standard procedure. TSR is calculated as the ratio of the average wet indirect tensile strength (ITS) to the average dry ITS. TSR is usually expressed as a percentage, but not always, and is sometimes referred to as "retained strength." Table 3.15 shows the TSR test results. Figure 3.21 shows the TSR test device.

Table 3.15. TSR Test Results

GCS Condition & Number	RR-based FPM				CycL-based FPM			
	Voids (%)	Avg. Voids (%)	ITS (psi)	Avg. ITS (psi)	Voids (%)	Avg. Voids (%)	ITS (psi)	Avg. ITS (psi)
Wet-1	7.34		79		7.28		91	
Wet-2	8.04		77		7.41		90	
Wet-3	7.57	7.65	80	79	7.14	7.28	93	91
Dry-1	7.57		124		7.22		122	
Dry-2	7.81		123		7.29		122	
Dry-3	7.52	7.63	123	123	7.28	7.27	124	123
			TSR (%)	63.9			TSR (%)	74.3

The test results shown in Table 3.15 indicate that the RR FPM is more prone to stripping than the CycL FPM; a difference in the TSRs of 10% seems pretty conclusive in this regard. However, the TSR test is highly variable. The most recent study on developing precision statements for the TSR test report a single-operator standard deviation (i.e. 1s) of 3.3%, and the single-operator acceptable range of two results (i.e. d2s) as 9.3% [103]. Although the precision limits have not yet been adopted by AASHTO, the report verifies what has been widely recognized for some time now; the TSR test variability is problematic and a better method of evaluating the moisture-susceptibility of a FPM is needed. The Hamburg wheel-track test is increasingly the preferred alternative to the TSR in assessing stripping potential [104] [105] even though there are no precision statements for the Hamburg test at this time [100].

Figure 3.21. Tensile Strength Ratio Test Device

Table 3.15 also shows that the RR GCS average % air voids for both the wet and dry sets were slightly out of specification on the high side, and were about 0.35% higher than the average % air voids of the CycL GCSs. One could argue that this higher void content allowed for greater penetration of the water into the RR wet GCSs and resulted in greater moisture damage. However, an observation made during the hot water bath conditioning procedure may also explain the lower TSR for the RR FPM. When the hot water bath lid was raised just prior to transferring the specimens to the room temperature bath, the odor of the RR was unmistakable. It is speculated that there was some dissolution of the RR by the 60°C water during the 24 hour submergence period. This observation was not totally unexpected. One must remember that the RR was extracted from the bulk rubber using acetone, but the rubber was extracted from the guayule shrub using a water-based process. The issue of potential water solubility of the RR under certain conditions was always a concern. It may be instructive that the 50°C water temperature during the 7 hour long Hamburg test did not seem to negatively impact the results whereas the 60°C water temperature during the 24 hour TSR conditioning procedure may have had the opposite effect.

3.1.6.4 Low-temperature flexural creep stiffness testing. A relatively new test was used to determine low-temperature flexural creep stiffness of the RR and CycL FPMs. Two documents were used as guidance in this exercise: a Utah DOT research report [106] and a NCHRP-IDEA report [107]. The test is essentially the same used to determine the low critical temperature of binders with two basic exceptions: the test specimens are FPM beams instead of binder beams, and the creep load is larger. The FPM beams are of the same dimensions as the binder beams (6.35 mm thick, 12.70 mm wide, and 127 m long) and, for this study, were cut from the center of the gyratory-compacted volumetric specimens.

Eight FPM beams were cut from each of the eight volumetric specimens resulting in 32 RR FPM beams and 32 CycL FPM beams. A masonry saw was used to cut a 20 mm thick disk from the center of each of the volumetric specimens, and then a wet tile saw was used to reduce each 20 mm thick, 105 mm diameter disk to eight FPM beams of the proper dimensions. The cutting and subsequent determination of the actual dimensions of the FPM beams were done at Missouri S&T while the BBR testing was performed at the MoDOT Central Laboratory. Figure 3.22 shows the 64 FPM beams.

Regarding test temperatures, the Utah report draft protocol states, “For quality control purposes the single test temperature shall be 10 ºC above the specified binder grade used in the mixture. For performance prediction at least 3 temperatures shall be used at 6 ºC intervals. The test temperatures of 4 ºC, 10 ºC, and 16 ºC above the specified binder grade used in the mixtures have been successfully used. Other temperatures can also be used depending on the project requirements.” For this investigation, testing was performed at -12°C to meet the quality control criteria discussed above, and -18°C to be able to do a temperature-dependency analysis. Because the beam specimens can only be tested once, four of the beams cut from each of the eight volumetric specimens were tested at -12°C and the other four were tested at -18°C. Test results of interest for this comparative analysis were the stiffness and the m-value at 60 seconds of creep load which were obtained from the BBR software output. The results are shown graphically in Figures 3.23 and 3.24. It should be noted that “R” identifies the RR FPM and “C” identifies the CycL FPM. The numbers “1&2” mean that all valid data from the testing of both batches of each FPM are included in the trendline determination.

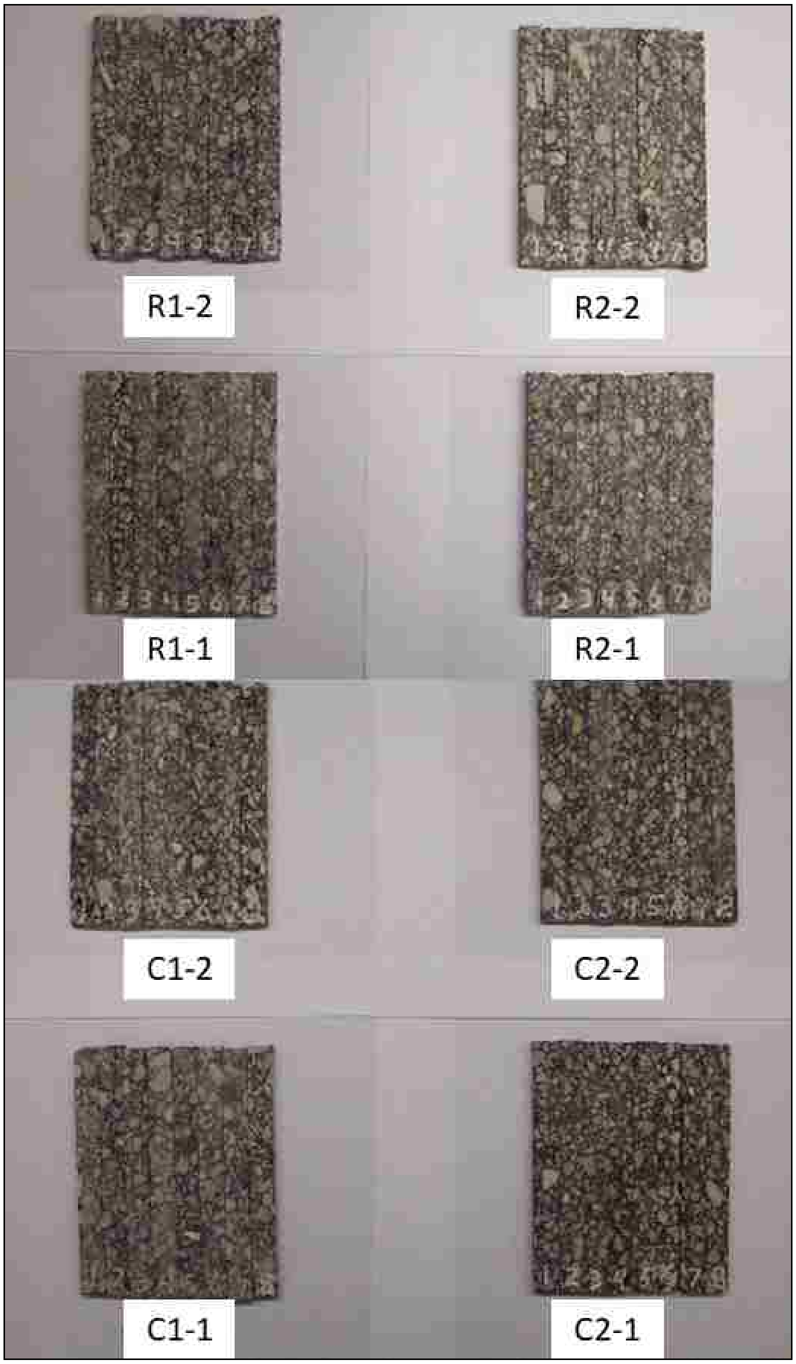


Figure 3.22. Cut FPM BBR Beams

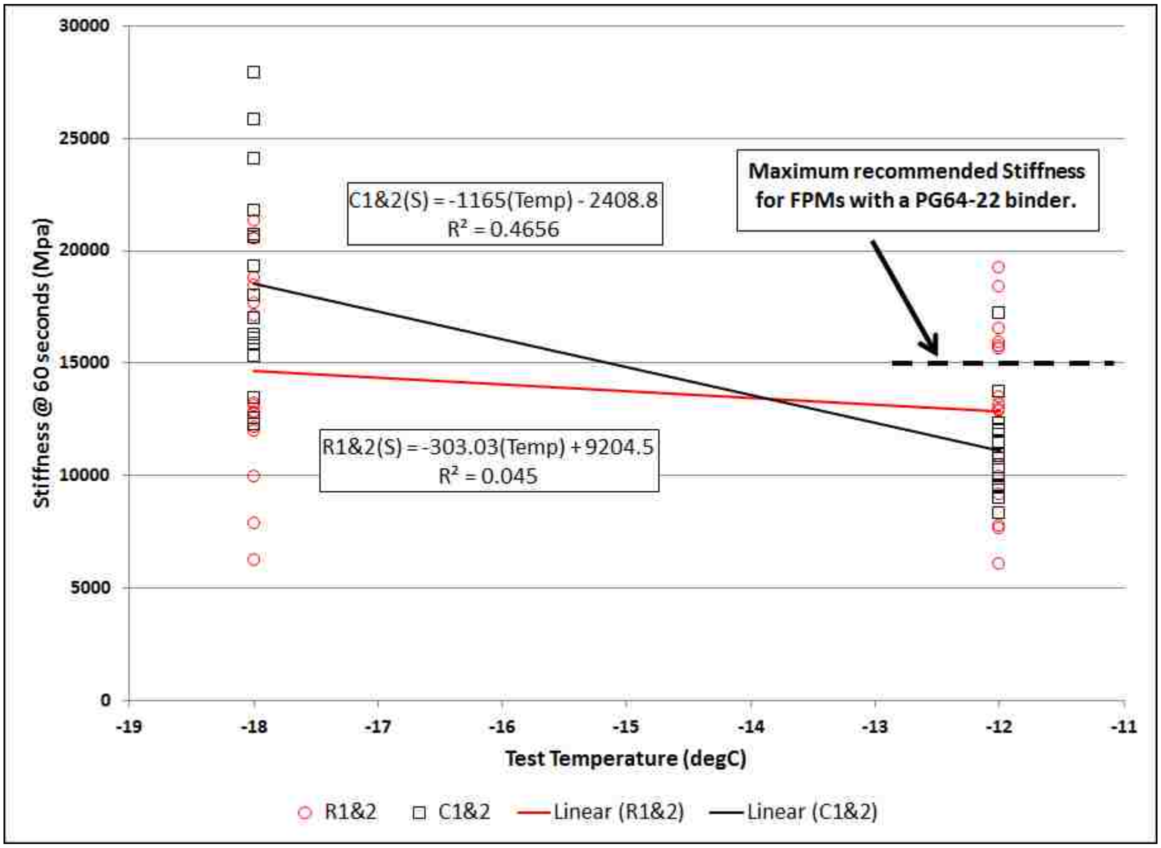


Figure 3.23. RR vs. CycL Low-Temperature Flexural Creep Tests: Stiffness

There are only 63 data points reflected in Figures 3.23 and 3.24. One beam test was discarded due to testing irregularities. The Utah DOT report recommends testing five beams per treatment combination and if the coefficient of variation (CV) for those five repeated measurements is greater than 15%, one should check for an outlier, remove it if it exists, then recalculate CV for the four remaining beams. If CV is still greater than 15%, the entire test is invalid. If this precision recommendation had been applied to the data in this investigation, a majority portion would have been invalid. Personnel at the MoDOT Central Lab indicated that test data they have been collecting for their purposes also sometimes violates this 15% CV level. Therefore, this recommended precision statement was disregarded in this investigation. It is also important to note that the referenced NCHRP-IDEA report concluded that differences in % air voids have no significant effect on creep stiffness of FPMs at low temperatures. No attempt was made during this exercise to verify this conclusion.

Figure 3.23 shows trends of increasing stiffness variability (at 60 seconds of creep load) as the temperature decreases, higher variability in the RR stiffness data relative to the CycL data as measured by R^2, and interestingly, a flatter stiffness – temperature trendline slope for the RR FPM. A check on the flatter RR FPM stiffness – temperature slope was performed by fitting trendlines individually to each set of FPM batch data. The result corroborated the trend shown in Figure 3.23.

The increasing variability at decreasing temperature is reasonable. Greater beam stiffness at lower temperatures exacerbates the effect of flaws within the aggregate/binder structure. It is not as clear as to why the RR data is more variable relative to the CycL data. Since the beams were cut from the volumetric GCSs, the variability issue might derive from the condition of the GCSs. The flatter stiffness – temperature slope for the RR FPM trendline is curious. As an outlier analysis was not performed on the data, as discussed in the previous paragraph, it could be that some of the stiffness data points in the RR dataset at both temperatures were actually outliers with high leverage that skewed the mean stiffness per temperature in the direction that would result in the flatter trendline.

The Utah report also has recommended maximum stiffness and minimum m-value limits. The report states, “The average stiffness of the mixture at 60-seconds and at a temperature of 10 ºC above the performance grade of the binder shall not exceed 15,000

MPa; the average m-value at the same loading time and temperature shall not exceed 0.12.” Note that the last part of this statement could be worded more specifically to indicate that 0.12 is a recommended “minimum” value. As indicated in Figure 3.23, both the RR and CycL FPMs meet the maximum stiffness recommendation. Additionally, even though the RR trendline is slightly higher than the CycL trendline at -12°C, a two-sided t-test (blocked across the different FPM batches) showed that the 60 second creep stiffness of the RR and CycL FPMs are not significantly different, based on a significance level of 5% (i.e. alpha=0.05).

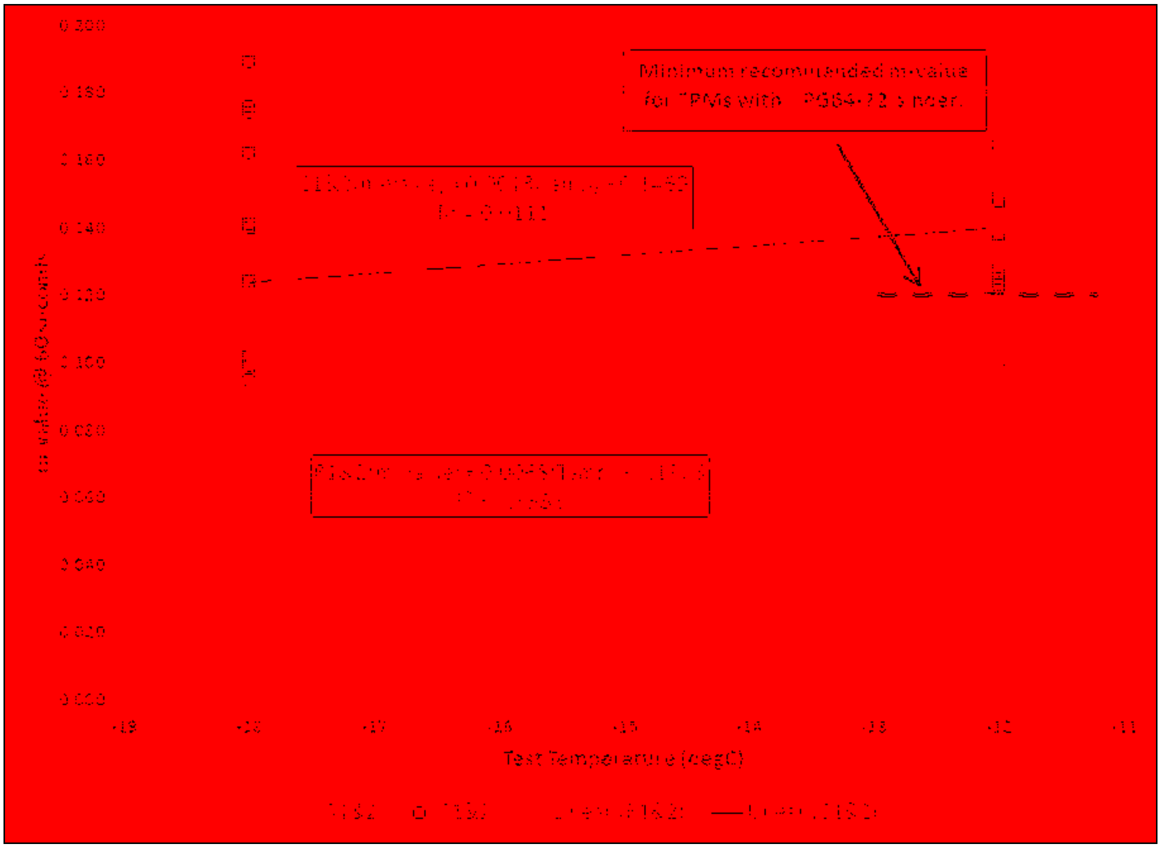


Figure 3.24. RR vs. CycL Low-Temperature Flexural Creep Tests: m-value

Although stiffness is an important and specified parameter to consider when evaluating the low temperature cracking potential of a FPM, the m-value is usually the parameter that controls when checking both parameters against the specifications, for example, in binder testing. Remember that the stiffness (or modulus) is a measure of a beam's resistance to deflection (strain), whereas the m-value is a measure of the rate-of-change of stiffness with time; i.e. as the temperature decreases, the thermal shrinkage stresses are dissipated quicker as the m-value increases [99].

Figure 3.24 shows trends of increasing m-value variability (at 60 seconds of creep load) as the temperature decreases (the same trend as stiffness), and higher variability in the CycL m-value data relative to the RR data as measured by R^2 (opposite of the stiffness trend). The trendline slopes are approximately the same, but the relative position of the CycL trendline to the RR trendline indicates that the CycL FPM has superior stress relaxation properties than the RR FPM.

Again, as with all of the other comparative analyses presented in this report, an analytical result such as this does not necessarily mean that the RR cannot be used as a RA. For example, as shown in Figure 3.24, even though the RR FPM m-value trendline at -12°C is slightly below (i.e. "exceeded") the recommended minimum, adjustment of the blended binder proportions of the mix design could increase the m-value.

3.1.6.5 Summary of FPM design, production, and testing. A summary of the results for this section is given in the following bullet-point list:

- The final FPM % air voids were slightly high of specification, but fell in the generally acceptable range of 4 ± 1%. VMA was within 0.1% of meeting specification. VFA met specification.

- The FPM utilized 53% reclaimed aggregate (from the RAPs and RAS) which means major cost savings.
- Only 0.23% of the total FPM mass (or 5.62% of total binder mass) was virgin PG64-22 binder, a result that relates favorably to the IDEA project concept which was to produce a successful FPM with little-to-no virgin petroleum-based binder.
- The rest of the binding materials was reclaimed RAP/RAS binder (i.e. more cost savings) and RR as the RA.
- The results of the Hamburg wheel-track testing showed that the RR-based FPM performed as well as the CycL-based FPM, conservatively speaking.
- The Tensile Strength Ratio (TSR) testing indicated that the CycL-based FPM performed somewhat better than the RR-based FPM. Speculation was that some dissolution of the RR may have occurred during the hot water bath conditioning which may have affected the indirect tensile strength of the RR-based FPM TSR specimens. Also, % air voids of the RR-based FPM TSR specimens were slightly out of specification on the high side, and they were about 0.4% higher than the CycL-based FPM TSR specimens.
- The non-standard test, Low-Temperature Flexural Creep Stiffness of the FPM beams, indicated a fair comparison between the RR-based, and CycL-based FPMs at -12°C.

3.1.7. Yulex and USDA-ARS Era Summary. After viewing a 2004 documentary on rubber that included a short piece on the guayule plant, contact was made with Dr. Francis Nakayama of the USDA in 2006 and the first samples of guayule rubber and resin were obtained. The resin was of particular interest and became the focus of further investigation. A NCHRP-IDEA research contract was awarded in 2009 to evaluate the USDA-supplied guayule resin as a RA in FPMs with high contents of RAP and/or RAS.

Short supplies of the USDA-supplied resin and insufficient information and time needed to replicate the resin, however, forced a change in the scope of the IDEA project. The decision was made to extract resins directly from guayule plant feedstocks. Those feedstocks included chipped whole-shrub and post-latex-extraction bagasse, and were supplied by the USDA and the Yulex Corporation. Ultimately, eleven different combinations of guayule-based feedstock, solvent(s), and extraction procedures were investigated.

Of the eleven extracts evaluated, two were selected for further investigation: the RR and the LF. These were compared to two commercially-available, petroleum-based RAs, CycL and a PG52-28 binder, respectively. Test results showed that the LF was not well suited as a RA, but could prove to be useful as a polymer-modifier to improve high-temperature performance of FPMs. Therefore, the focus of the study turned solely onto the RR.

The RR performed as a RA in every respect except that it suffered some moderate, out-of-specification mass loss when blended with petroleum-based reclaimed and virgin binders at the proportions selected for the binder grade verification and FPM testing. Though the RR did not always compare identically with the CycL in a binder blend or in a FPM, this does not mean that the RR could not be used as a RA.

Despite the fact that the Yulex Corporation is not pursuing commercialization of guayule plant products at this time, the test results obtained during the NCHRP-IDEA project were encouraging and showed that compounds from the guayule plant could be used as binder modifiers in FPMs. Dissemination of these results has led to the interest by companies such as Bridgestone Americas and PanAridus to pursue the use of guayule resins as binder modifiers in FPMs.

3.2. BRIDGESTONE AMERICAS AND PANARIDUS ERA

The guayule resins discussed in this section were extracted through simultaneous extraction processes using a proprietary mixture of acetone and hexane as the solvents. Nevertheless, the Bridgestone Americas (BSA) and PanAridus crude, process run resins are considerably different. Limited testing was performed on both process run resins and a few other guayule rubber (GR) extraction by-products supplied by the two companies. The results are presented in the following sections.

3.2.1. PanAridus. The first solvent-extracted resin sample was delivered by PanAridus to Missouri S&T on May 29, 2015. This first sample, designated as PA1, had similar viscosity, color, and odor as the original USDA-ARS de-rubberized resin sent by Dr. Nakayama in 2006. However, PA1 contained a considerable amount of low molecular weight (LMW) GR that would float to the top of the sample if left undisturbed for a sufficient length of time. The second PanAridus resin sample, designated as PA2, arrived on February 16, 2016. PA2 was a laboratory improved version of PA1 in that it had less LMW GR and residual solvents (hexane and acetone). The third sample, designated as PA3, was delivered on July 12, 2016. PA3 was a newer process run resin based on the improvements in PA2.

Because the testing of the PanAridus resins was pro bono, test methods were not always performed strictly by the specifications. This work was a real-time collaboration in which a basic, cursory evaluation of the different resins was performed and the results were reported back to PanAridus. Testing included gas chromatography – mass spectrometry (GC-MS), Brookfield rotational viscosity [87], a modified-version of the standard test method ASTM D 7173, Separation Tendency of Polymer from Polymer Modified Asphalt [108], and two non-standard examinations: RAP dispersal in the resin over time (i.e. resin-as-solvent), and dissolution of the resin in 60°C water for an extended period of time.

The only investigation on the PA1 resin involved observing any dispersal or dissolution of RAP in a container of the resin. This exercise was called the resin-as-solvent test. Figure 3.25 shows the steps in starting the exercise.

As shown in Figure 3.25, a backlit Petri dish was used as the container for viewing purposes. The four numbered steps took a very short amount of time to complete, and as one can see in Step 4, unidentified compounds in the RAP had already started to disperse throughout the resin. Figure 3.26 shows the same setup but a 7 month time period had elapsed between the two pictures.

As can be seen in Figure 3.26, long-term continual dispersion of RAP compounds (admittedly, unidentified at this point) occurred. Speculation is that the monoterpenes in the resin act as a solvent. As discussed earlier, Pinenes are major constituents in turpentine and Limonene is the basis of “citrus” cleaners. This result was encouraging, most notably in regard to the potential prolonged durability of in-service FPM binders/modifiers. The hope is that the resin can help alleviate premature age-hardening (oxidation) of the FPM binder through its apparent capability to dissolve and disperse, perhaps, aggregations of asphaltenes and/or petroleum resins over time. Also, and more likely, high monoterpene content resin may be useful as a pre-treatment to RAP and RAS. The application of the resin to RAP/RAS prior to final mixing with heated virgin binder and aggregates may promote a more thorough blending of the reclaimed RAP/RAS binders with the virgin binder, which is of concern to asphalt technologists and producers.

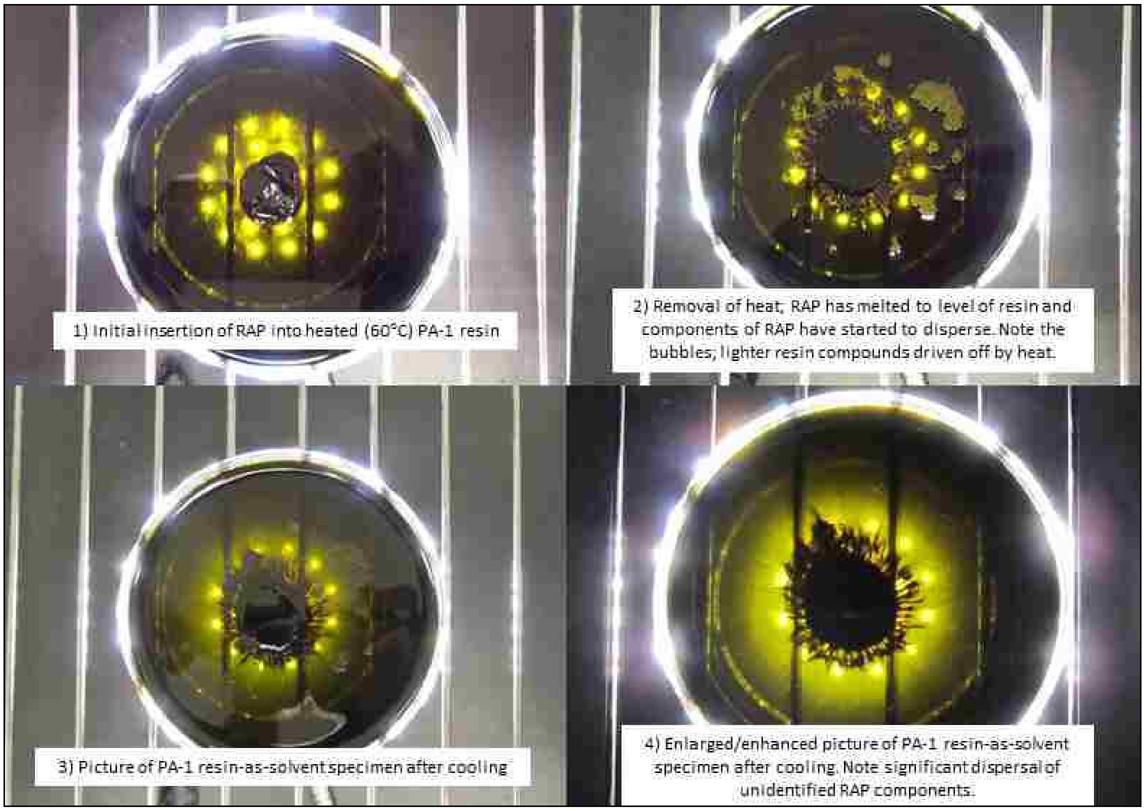
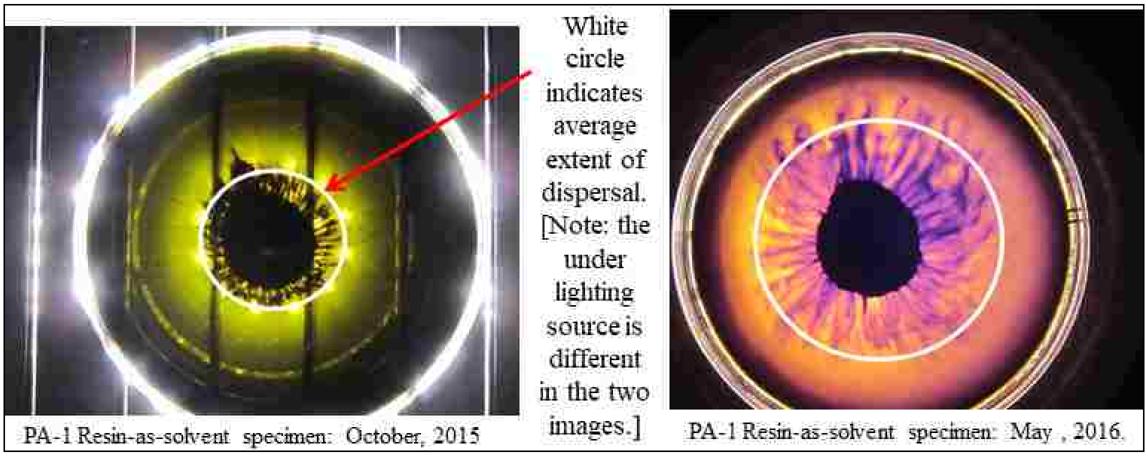


Figure 3.25. PA1 Resin-as-Solvent Test



White circle indicates average extent of dispersal. [Note: the under lighting source is different in the two images.]

PA-1 Resin-as-solvent specimen: October, 2015

PA-1 Resin-as-solvent specimen: May , 2016.

Figure 3.26. PA1 Resin-as-Solvent Test, Extended Time Lapse

The first test results to be presented on PA2 are the GC-MS results. PanAridus indicated that their crude, process run resin usually had about 10% LMW GR in it. However, significant effort had gone into removing as much LMW GR from the PA2 sample as possible. PanAridus also indicated that the PA2 sample had 5 to 10% more of the volatile terpenes like α- and β-Pinene in it relative to their crude, process run resin. Figure 3.27 shows the GC-MS chromatograph for PA2.

Figure 3.27 shows GC-MS results for PA2 that were expected based on the initial observations of the resin and its similarity to the original de-rubberized resin supplied by Dr. Nakayama: a high concentration of monoterpenes ($C_{10}H_{16}$) α- and β-Pinenes, Limonene, and Camphene. Also, there is a significant presence of sesquiterpenes ($C_{15}H_{24}$) Caryophyllene and Elemene, although these compounds are not annotated. The presence of acetone and hexane was also expected.

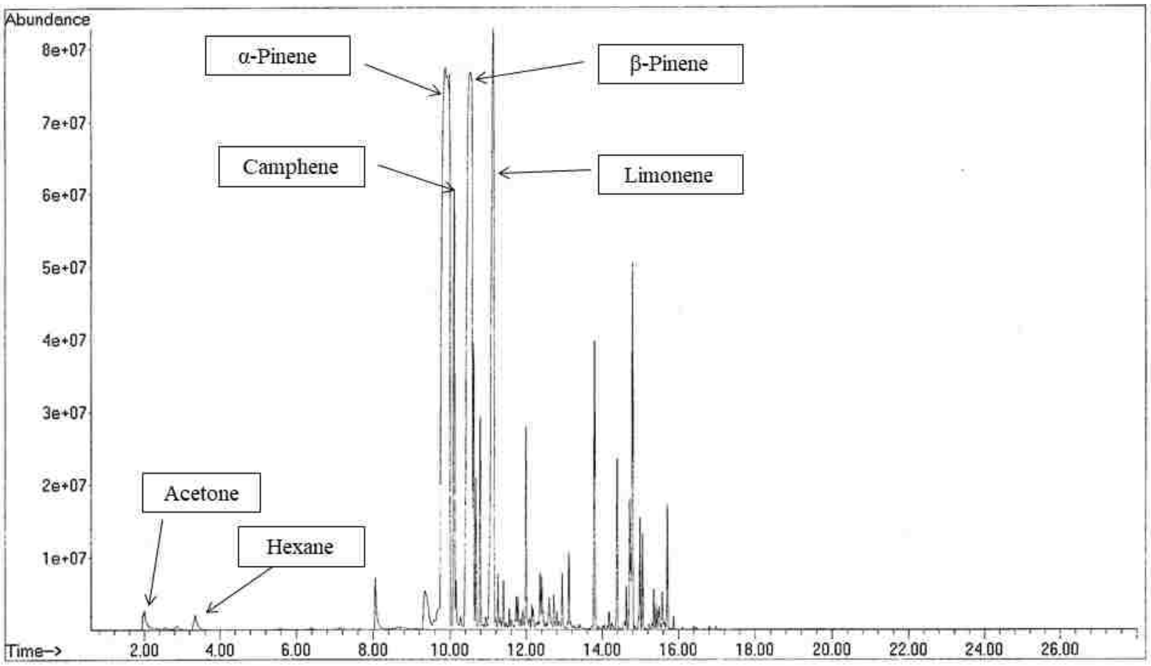


Figure 3.27. PA2 GC-MS Results

It was known before receiving confirmation from PanAridus that there was a significant amount of LMW GR in the PA1 resin simply by observing the sample over time; the GR would float (separate) to the surface of the sample. When the PA2 resin was delivered, and even though PanAridus stated it removed the LMW GR from that sample, it seemed worthwhile to evaluate the compatibility of any trace or residual LMW GR in the PA2 resin with petroleum-based binders. Therefore, a blend of PG64-22 (50%), RAP2 (46%), and PA2 (4%) was generated using only heat and stirring utensils; i.e. the Brookfield mixer setup was not used in any of the Bridgestone Americas/PanAridus Era testing. Discussion of how the blend percentages were determined will follow presentation of the results.

Using this blend, a modified-version of the ASTM D 7173 separation tendency test was performed. Specimen preparation followed the standard test procedure. The blend was put in a sealed aluminum tube and conditioned in a vertical position for 48 hours at 163 ± 5°C. After conditioning, the tube was put in a freezer for the specified period of time, the top and bottom thirds were cut from the tube and those thirds were evaluated for differences.

Regarding the standard test method, MoDOT still specifies performing the separation test on original PG binder [109]. However, MoDOT specifies an older version of the test, ASTM D 5976 (discontinued). The MoDOT specification requires determining G* (complex shear modulus) using a DSR on the top and bottom thirds of the specimen, computing the percent difference in the G*s, and comparing that percent difference to specification criteria. For example, MoDOT requires that the percent difference in G* values does not exceed 10% on original binders that have absolute temperature spreads of 92, 98, or 104°C; i.e. usually polymer-modified binders. However, for this cursory examination of the PA2 resin, the viscosity of the top and bottom thirds was determined using the Brookfield viscometer and a percent difference evaluation was performed. Table 3.16 shows the test parameters and results.

Referring to Table 3.16, the percentage of the virgin petroleum-based binder, PG64-22, was set at a minimum of 50% to stay within real-world expectations during any future field work in Missouri, and its viscosity at 135°C was chosen as the target viscosity of the blend. Viscosities of the PG64-22, RAP2, and PA2 at 135°C were 410, 2770, and 36 centipoise, respectively. It should be noted that the PA2 viscosity was estimated through extrapolation as the Brookfield viscometer did not have the capacity to measure viscosities that low.

Table 3.16. PA2 Blend Separation Test Parameters and Results

Blend Components and Proportions (mass %)			Blend Viscosity (centipoise) at 135°C	Separation Testing (Viscosity: centipoise)			
PG64-22 (orig)	RAP2	PA2		Top 1/3 at 135°C	Bottom 1/3 at 135°C	Top 1/3 at 165°C	Bottom 1/3 at 165°C
50.0	46.0	4.0	663	741	742	180	180

The same weighted-average calculation method used for determining G_{sb} of a blend of aggregates for FPM mix design purposes was used to estimate viscosity of a blend of binder materials. Substituting viscosities of each blend component for the G_{sb} of the individual aggregate fractions, the percentages of the RAP2 and PA2 were toggled until the calculated weighted-average was close to 410 centipoise, the target blend viscosity. Several trial runs were performed using this method and slightly different RAP2 and PA2 percentages to attempt to home in on the target viscosity. As one can see in Table 3.16, the viscosity of the actual blend determined at 135°C was 663 centipoise, which, after a few attempts, was surprisingly close to the target. This method of utilizing a weighted-average of viscosities to determine blend percentages is a topic for future research.

Regarding the separation testing results shown in Table 3.16, there was no apparent difference in the top and bottom thirds of the blend, implying that there was no separation of the GR in the PA2, provided there was actually any present. Also, it should be reiterated that standard protocol calls for determination of G*, a more sensitive test than viscosity, to evaluate potential separation. G* would be a more sensitive test and may have detected any separation had it occurred. Nevertheless, there were things learned during this exercise that would prove to be useful later during the evaluation of the Bridgestone Americas guayule-based materials.

The next set of results to present corresponds to an issue experienced during the TSR testing of the RR-based FPMs in Section 3.1.6.3. To review, the conditioning of the RR TSR specimens in the 60°C water bath for 24 hours caused concern because when the water bath lid was raised after the 24 hour period, one could distinctly smell the RR. The assumption was that the prolonged exposure to the high temperature water caused some dissolution of the RR in the blended FPM binder. That assumption was strengthened when the RR TSR results turned out to be considerably poorer than the CycL-based FPM TSR test results. Therefore, to determine the possibility of this issue occurring with the solvent-extracted resins, a simple test was performed in which a small sample of each of the two process run resins were put in 500 ml Erlenmeyer flasks, covered with water, and put in a 60°C oven for 24 hours. Figure 3.28 shows the results of this exercise on the PA2 resin.

There is some dissolution/separation of unidentified compounds shown in Figure 3.28, but this was not unexpected. It is possible that these are lighter compounds, such as the monoterpenes, that would be driven off anyway as a result of heating during FPM production. Although not pursued at the time, a follow-up exercise might be to create a blend similar to that discussed above during the separation testing and perform the 60°C dissolution test. Heating the blend to mix it would drive off some of the lighter compounds in the resin, and if after the dissolution test there was no material floating on the water in the flask, one could surmise that the floating material was likely monoterpenes.

Figure 3.28. PA2 60°C Dissolution Test: 6 hours (top), 24 hours (bottom)

Figure 3.29 shows the viscosity testing results on the PA2 and PA3 resins. The viscosity-temperature curves of the RR and CycL are included for comparison purposes. It should be noted that the PA3 resin was the latest PanAridus' process run resin supplied to Missouri S&T during this period of collaboration. PanAridus reported that the PA3 sample had about 5% LMW GR whereas the PA2 sample had, reportedly, 0%.

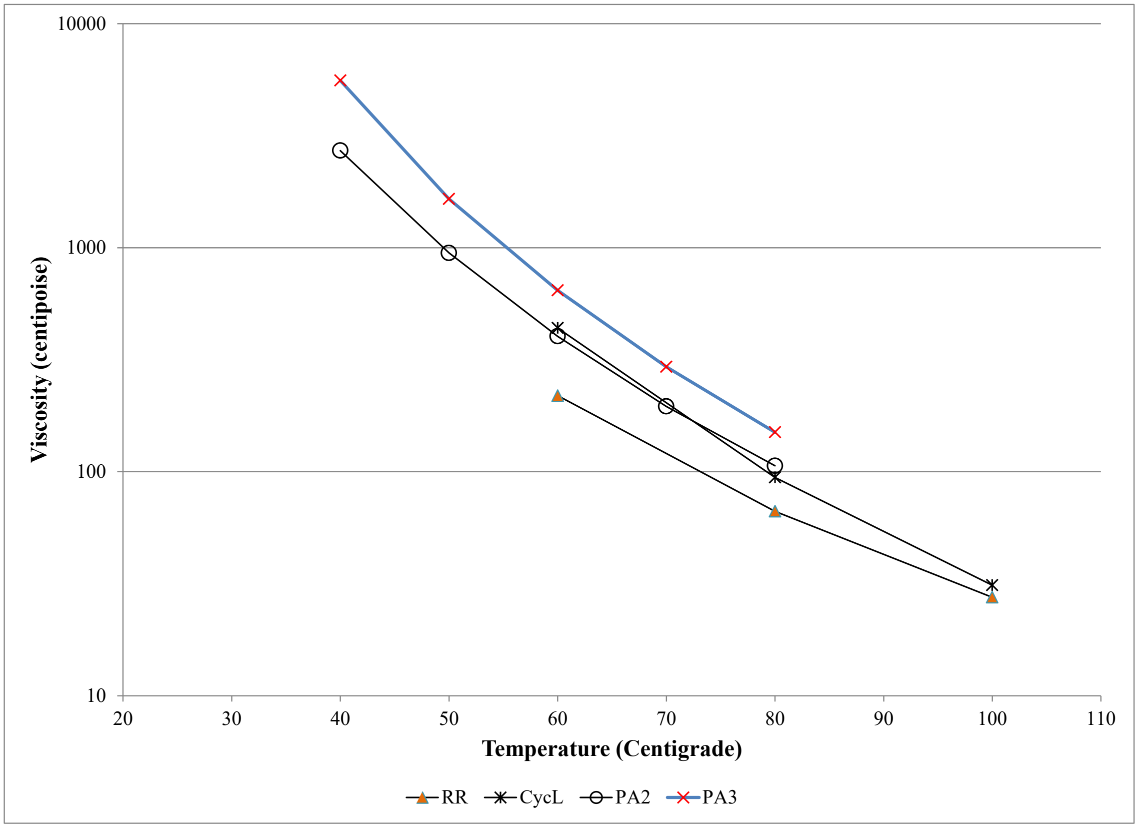


Figure 3.29. PA2 and PA3 Viscosity Results

The CycL and PA2 viscosity-temperature curves line up almost on top of one another, a result that would make them the next two candidates for comparisons in a more in-depth investigation. The PA3 resin is slightly more viscous than the PA2 resin which is logical due to the elevated LMW GR levels in PA3, according to PanAridus.

3.2.2. Bridgestone Americas. Bridgestone Americas (BSA) supplied several different guayule-based materials during the course of the collaboration. The first shipment contained several quart cans of the crude resin by-product of the rubber extraction at the BSA Biorubber Process Research Center, and a multi-pound block of the crude resin that had been processed (e.g. heated) to remove most of the lighter, more volatile fractions. For identification purposes in this section, these two items are designated as BV (Bridgestone with volatiles) and BNV (Bridgestone no volatiles), respectively. The second shipment contained a small sample of the BNV resin with a moderate amount of residual rubber (BMR), and another similarly-sized sample of BNV resin with a larger amount of residual rubber (BHR). Laboratory evaluations were performed on the BV, BNV, and BMR materials. The same five ad hoc examinations performed on PanAridus materials were performed on some, but not all, of the BSA materials.

It is important to point out that the BSA process run or crude resin has much more LMW GR in it than the PanAridus crude resin. This fact was abundantly clear when the lid was removed from the first BV quart container inspected after delivery. The resin will string out substantially, at room temperature, indicating a significant presence of elastomeric materials.

Figure 3.30 shows the results of the dissolution testing on the BV and BNV resins. The effect pre-heating the BV and driving off the volatiles will have before dissolution testing is shown in Figure 3.30. There are some floating compounds in the BV flask while the BNV flask water is still clear after 24 hours at 60°C. This phenomenon helps corroborate the assumption made about the PanAridus dissolution test results, that lighter, more volatile compounds can be extracted at elevated temperatures in the presence of water. Suggested follow-up work would be to collect samples of the floating materials in both the PanAridus and BSA dissolution testing and perform GC-MS and/or other compound-characterization testing to identify them.

Figure 3.30. BV and BNV Dissolution Test at 60°C for 24 Hours

GC-MS testing was performed on the BV and BNV resins. The BV was tested after pre-heating the GC-MS specimens to two different temperatures: 25 and 60°C. Figure 3.31 shows the BV GC-MS results after pre-heating to 25°C.

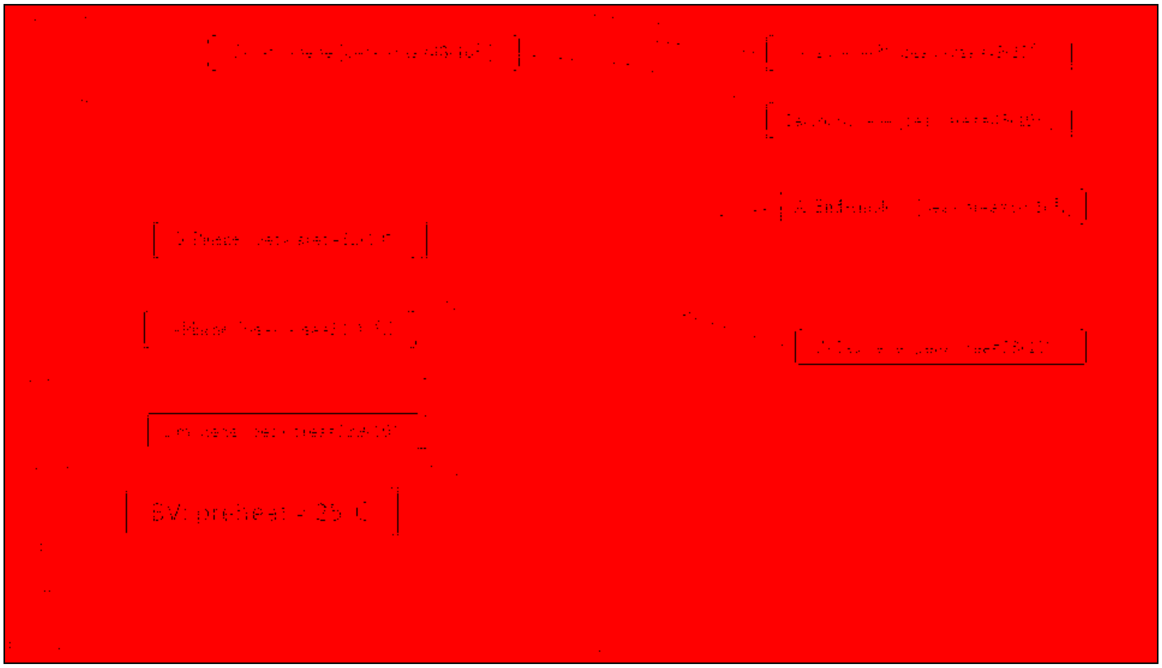


Figure 3.31. BV Resin GC-MS Results (Pre-heated to 25°C)

The three common monoterpenes (C_{10}), the Pinenes and the Limonene, are present but in reduced abundance relative to the PanAridus resin Pinenes and Limonene, and relative to the five other identified compounds in Figure 3.31, all sesquiterpenes (C_{15}) or terpenoids (e.g. A-Eudesmol is an oxygenated sesquiterpene). Figure 3.32 shows the BV resin GC-MS results but after the specimen was pre-heated to 60°C. Figure 3.33 shows the GC-MS results for the BNV resin pre-heated to 25°C.

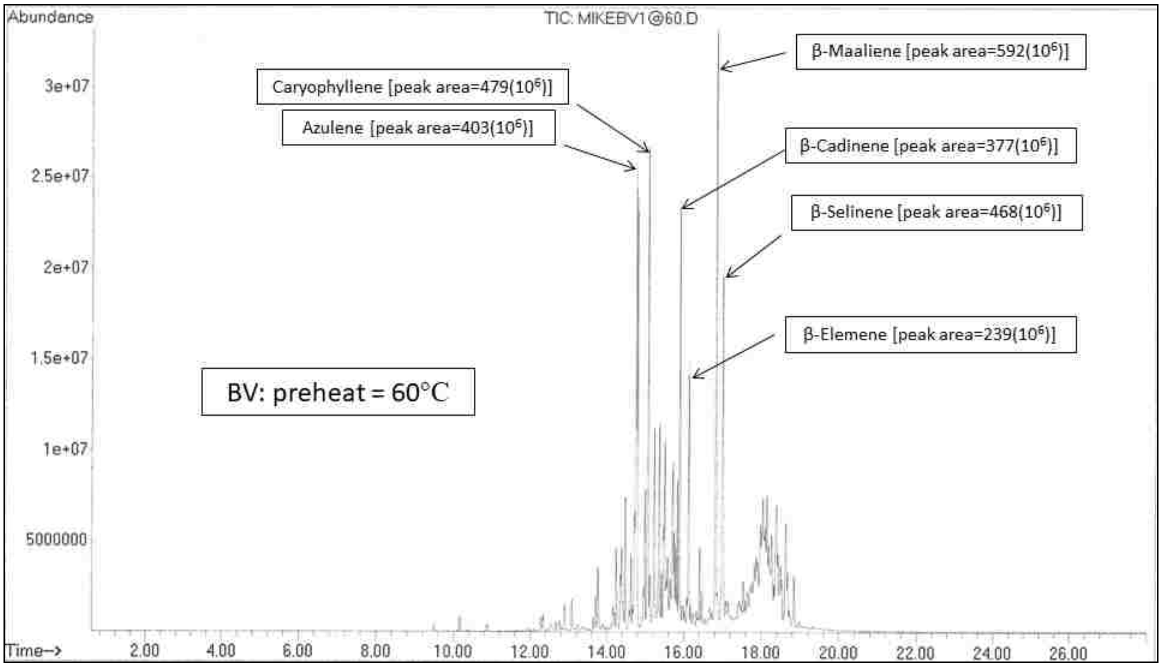


Figure 3.32. BV Resin GC-MS Results (Pre-heated to 60°C)

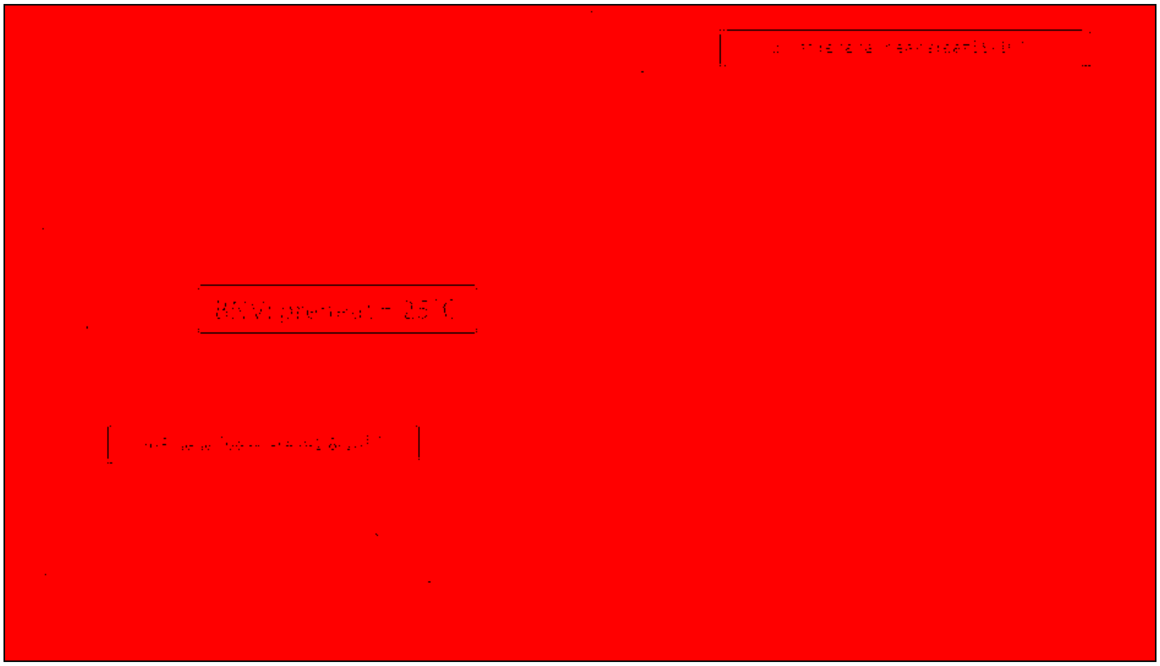


Figure 3.33. BNV Resin GC-MS Results (Pre-heated to 25°C)

As one can see in Figure 3.32, the monoterpenes were driven off by preheating the BV resin. Only the heavier sesquiterpenes were detected. The results in Figure 3.33 simply reiterate the effect of heating the resins, at any time: the lighter compounds are reduced in abundance.

The resin-as-solvent exercise was carried out on the BV and BNV resins, as well. Figure 3.34 shows those results.

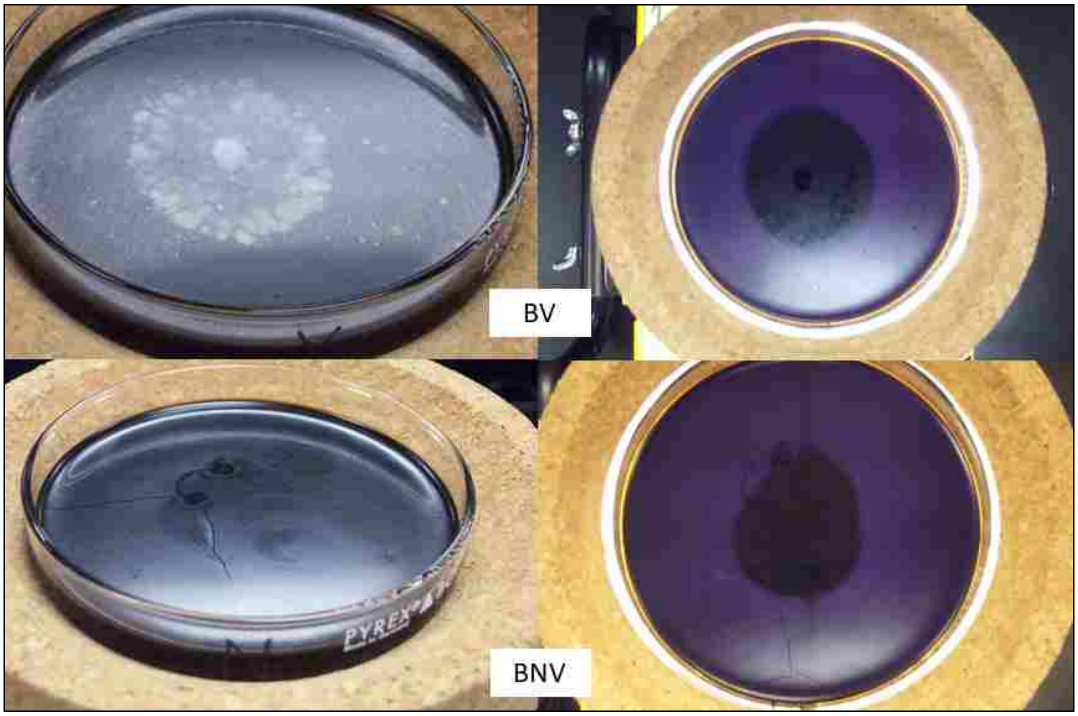


Figure 3.34. BV and BNV Resin-as-Solvent Test

The two pictures per specimen in Figure 3.34 are simply to give one a better view of the surface and as backlit. Neither the BV nor the BNV specimens showed any dispersal over an extended period of time. This was not unexpected as the monoterpene (i.e. the solvent) content was significantly reduced relative to the PanAridus resin. It is a little hard to distinguish, but the BNV specimen actually cracked after cooling to room temperature. To review, the specimens were slightly heated so that when the RAP particle was placed in the resin, the RAP particle would melt slightly and level out in the resin.

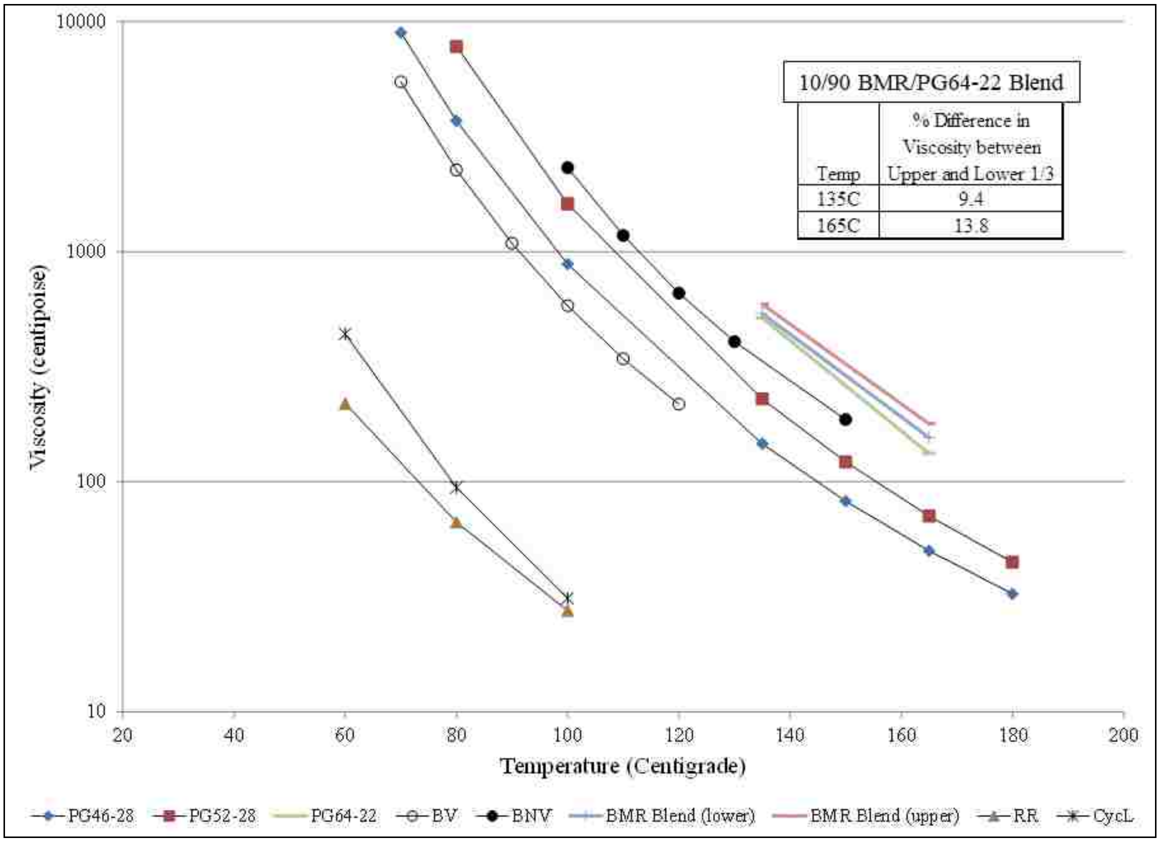
Separation (compatibility) testing was performed on three different blends using the BSA materials: The BV, BNV, and the BMR. Table 3.17 shows the results of the BV and BNV separation testing.

Table 3.17. BV and BNV Blend Separation Test Parameters and Results

Blend Components and Proportions (mass %)				Blend Viscosity (cp) at 135°C	Separation Testing (Viscosity: centipoise)			
PG64-22 (orig)	RAP2	BV	BNV		Top 1/3 at 135°C	Bottom 1/3 at 135°C	Top 1/3 at 165°C	Bottom 1/3 at 165°C
50.0	37.0	13.0	0.0	512	559	553	151	150
50.0	12.0	0.0	38.0	376	396	397	122	122

Referring to the separation test results given in Table 3.17, all of the procedural particulars that were followed for the PA2 analysis (Table 3.16) were followed for the BV and BNV analysis. As in the PA2 analysis, the target blend viscosity was 410 centipoise. The results shown in Table 3.17 show no indication of separation in the blends, as proportioned.

However, separation testing was also performed on a blend of the BMR (BNV with moderate amount of GR) and PG64-22 binder. The blend consisted of 10% BMR and 90% PG64-22, by mass. The results are given in the form of a viscosity plot, shown in Figure 3.35.



10/90 BMR/PG64-22 Blend

Temp	% Difference in Viscosity between Upper and Lower 1/3
135C	9.4
165C	13.8

Figure 3.35. BV, BNV, and BMR Blend Viscosity and Separation Testing

There are viscosity-temperature curves for several materials shown in Figure 3.35 for comparison purposes. It is interesting to note the position of the BV and BNV curves relative to the softer PG binders PG46-28 and PG52-28. The BNV is considerably more viscous than the BV, which is logical considering the lighter compounds in the BV were driven off through heating to create the BNV resin.

The results from the separation testing on the BMR/PG64-22 blend are shown in the form of three curves identified in the plot legend. It is not unexpected that the blends are more viscous than the neat PG64-22 binder because the blends were subjected to high temperature as part of the separation test specimen preparation procedure. However, the viscosity between the upper third (BMR Blend (upper)) and the lower third (BMR Blend (lower)) of the separation specimen, at both temperatures, is considerably different. Percent difference was calculated as the difference between the measured values per temperature, expressed as a percentage of the average of those values. There are no known (at least at this time) percent difference criteria for viscosity testing in a separation test, but 9.4% and 13.8% seem significant. This indicates that, like other polymer-modifiers for asphalt binder, separation can occur during high temperature storage and, therefore, continual agitation is required. The BMR blend not only had a higher viscosity than the neat PG64-22 binder (which was, again, not unexpected), but it also changed the performance by flattening out the viscosity-temperature curve, somewhat, relative to the neat PG64-22, which is a good thing. A flatter curve means the blend is less temperature susceptible; i.e. there is less change in viscosity for a given change in temperature.

3.2.3. Bridgestone Americas and PanAridus Era Summary. Although the testing was limited during this relatively short examination of the Bridgestone Americas (BSA) and PanAridus crude resins and other resinous materials, the results were very encouraging.

The high monoterpene content of the PanAridus crude resin indicates possibilities for use as a RA. The binder dispersal capacity seen during the limited testing suggests the monoterpenes could help the resin act as a pre-treatment to RAP/RAS to soften the age-hardened binder before addition to the mixing drum. This may allow for lower mixing temperatures, similar to a warm-mix technology.

The BSA crude resin is interesting in that, like the LF material, the low molecular weight rubber content could cause it to perform as a polymer-modifier, improving the high-temperature performance of a FPM while holding the low-temperature performance constant.

Although not related to test results, the fact that huge quantities of these resins are projected to be produced in the near future helps answer one of the most common questions asked by proposal reviewers and potential investors/stakeholders; “Will there be enough of this material available?” Hopes are high.

4. CONCLUSIONS

4.1. YULEX AND USDA-ARS ERA

Eleven different combinations of guayule feedstock material, solvent, and extraction/recovery process were investigated to determine the viability of the extract as a binder modifier. Out of the eleven resultant extracts, two were selected for further investigation: the acetone-extracted rubber resin (RR), and the hexane-extract (LF) from the waste-stream guayule leaves and attached stems. These were compared to two commercially-available, petroleum-based recycling agents (RAs), Cyclogen L and a PG binder PG52-28, respectively.

Results of binder-blending mixture experiments were useful for comparative analyses and necessary for FPM design. The experiments required creating, in total, almost 60 different blends of the RAP/RAS binders with the RR and LF, recreating those same blends but substituting the RR and LF with the appropriate petroleum-based RA or PG binder, testing each blend, and then generating response surface models (RSMs) using those test results. Conclusions from material characterization and the binder-blending experiments are as follows:

- Clay-gel chromatography testing verified that the pentane-soluble portion of the RR and LF pure blends (not blended with petroleum-based binder; i.e. 100% guayule-based material) met recycling agent specifications. Both contain polar and aromatic compounds, but less than 25% saturates by mass.
- The RR and LF pure blends are less temperature susceptible than the petroleum-based RAs and binders.

- The RR and LF pure blends suffer significant mass loss upon short-term aging at 163°C. Additionally, the RR can oxidize at room temperature if exposed to the air for prolonged periods of time, and may dissolve if exposed to hot water for prolonged periods of time.
- The absolute temperature spreads ($T_cH - T_cL$) for the LF-RAP/RAS blends were, to a large degree, significantly different than the proportionally-identical PG52-28-RAP/RAS blends. Eight of the nine LF-RAP/RAS blends in the analysis had, on average, a 12.3°C smaller temperature spread than the proportionally-identical PG52-28-RAP/RAS blends. This finding turned the remaining investigative effort solely onto the RR.
- Statistical analyses showed that the RR-RAP/RAS blends did perform the same as proportionally-identical CycL-RAP/RAS blends in terms of high-temperature stiffness (T_cH), but did not perform exactly the same in terms of cold-temperature cracking resistance (T_cL). The difference between the absolute temperature spread ($T_cH - T_cL$) for the RR-RAP/RAS blends relative to proportionally-identical CycL-RAP/RAS blends was small, but statistically different. Of the ten blends in the analyses, seven of the CycL-RAP/RAS blends had the larger absolute temperature spread (an average of 1.1°C) while three of the RR-RAP/RAS blends had a slightly larger temperature spread (an average of 0.3°C). So, although the RR-RAP/RAS blends did not perform exactly as the CycL-RAP/RAS blends in terms of T_cH and T_cL, this does not mean the RR cannot be used as a RA.

- A RR-RAP/RAS blend estimated by the RSM to meet PG64-22 binder specifications was produced and verification testing was performed. The RR-RAP/RAS blend met all PG64-22 specifications except mass change.

Using the verified binder blend, a RR-based FPM was designed, produced, and tested that met the gradation specification for a MoDOT BP-1 FPM, but did not quite meet all of the volumetric requirements. This FPM utilized 53% reclaimed aggregate (from the RAPs and RAS) and 47% virgin aggregate. More importantly, and in relation to the NCHRP-IDEA project concept, only 0.23% of the total FPM mass (or 5.62% of total binder mass) was virgin PG64-22 binder. The rest of the binder was RAP/RAS binder and RR. A CycL-based FPM using the same design process and proportions was also produced and tested for comparative analyses. Conclusions from the FPM performance testing are as follows:

- Standard Hamburg Wheel-Track testing, which specifies full submersion of the specimens in 50°C water during the approximately 7 hours of rut testing, was performed. The results indicated that the RR-based FPM performed as well as or better than the CycL-based FPM in regard to rutting and stripping (moisture damage) resistance.
- Standard Tensile Strength Ratio (TSR) testing, which specifies a 24 hour full submersion of the specimens in 60°C water, was performed. The results of this moisture-susceptibility test, however, indicated that the RR-based FPM may be more prone to stripping than the CycL-based FPM.
- A non-standard, but promising test protocol for determining low-temperature, FPM flexural creep stiffness was performed on the RR- and CycL-based

FPMs. At -12°C, statistical analyses showed that the creep stiffness of the RR-based FPM was not significantly different than the CycL-based FPM. However, the m-value of the RR-based FPM was statistically different (lower) than the CycL-based FPM m-value which indicates a somewhat higher cold-temperature cracking potential for the RR-based FPM relative to the CycL-based FPM.

4.2. BRIDGESTONE AMERICAS AND PANARIDUS ERA

The testing of the Bridgestone Americas (BSA) and PanAridus crude, process run resins and some additional BSA experimental resinous materials proved to be very encouraging in relation to planned future research. Although the investigation was ad hoc, and some of the test methods were non-standard, implications are good that the solvent-extracted guayule resins can be used as FPM binder modifiers. The conclusions are as follows:

- The PanAridus crude resin was higher in monoterpene content, but lower in low molecular weight (LMW) guayule rubber (GR) content than the BSA crude resin.
- Although the PanAridus resin's more volatile fractions (i.e. the monoterpenes) would likely be driven off during production of a warm or hot mix FPM, the concept of using the resin as a pre-treatment to RAP/RAS to soften the age-hardened binder prior to elevated-temperature mixing with virgin binder could be extremely beneficial to the industry.

- The solvent-extracted resins seem less likely to suffer moisture-related issues than the RR, a water-based extraction product.
- The significant quantities of LMW GR in the BSA crude resin, at least relative to the PanAridus resin, could be beneficial to the performance of FPMs in regard to high-temperature performance and elastic properties.
- Both crude resins would satisfy the basic purpose of a RA by reducing the viscosity of FPM with high RAP and/or RAS content.

4.3. ECONOMIC CONSIDERATIONS

This project verified that the guayule plant holds potential as a renewable, domestic source of bio-based binder modifiers such as resins, oils, and polymers.

The major advantage of the successful use of guayule resin as a RA is to reduce the costs of constructing flexible pavements by increasing the amount of RAP/RAS in FPMs. As discussed in the Introduction, a 2016 survey performed by the National Asphalt Pavement Association concluded, "... The use of recycled materials, primarily reclaimed asphalt pavement (RAP) and reclaimed asphalt shingles (RAS, either processed tear-off roofing shingles or roofing shingle manufacture waste), in asphalt pavements conserves raw materials and reduces overall asphalt mixture costs, as well as reduces the stream of material going into landfills. The combined savings of asphalt binder and aggregate from using RAP and RAS in asphalt mixtures is estimated at more than $2.1 billion" [1].

Adoption of the use of guayule resins in FPM will also increase the competition within the bio-based FPM binder modifier market, further reducing costs. Based on a recent phone survey of Missouri paving contractors conducted by the author, the price of the two most commonly used bio-based RAs, Hydrogreen and Evoflex, ranges from $0.60 to $1.00 per pound, depending on the volume purchased and distance shipped. BSA and PanAridus have claimed that once they are up and running on a commercial scale, they can compete in the bio-based RA market based on this price range.

It is important to point out the projected quantities of resin production that the industry partners foresee in the near future. Projections are as follows:

- Bridgestone Americas: "Commercial scale output of resin is envisioned in the range of 28,000 MT/year per factory…in the early to mid-2020s" [110].
- PanAridus: "On a commercial scale, PanAridus envisions ~80,000 tons of resin to be produced annually. The projected annual production could be 500,000 tons should the United States meet domestic natural rubber needs" [111].

Connecting the potential production of resin to the potential usage of resin can be done through an example calculation. Over the last few years, MoDOT has placed between three and four million tons of asphalt mixtures on its roadways each year. However, a product like guayule resin would not be required or would not be allowed in certain mixture types. For example, let's say only 25% of total asphalt tonnage is appropriate for resin addition, and the average resin addition rate is 0.5% by weight of mix. Based on three million tons of asphalt mixture placed in Missouri per year, 3750 tons of resin would be needed per year. Also consider that these numbers are based on looking only at state highway projects. County, city, and private asphalt projects have recently been a large portion of overall asphalt usage due to federal/state infrastructure funding issues.

The same 2016 NAPA survey cited above also concluded, “The estimated total production of WMA [warm mix asphalt] for the 2016 construction season was 116.8 million tons. This was a decline of 2.5 percent from the estimated 119.8 million tons of WMA in 2015, due largely to a 10.2 million ton decrease in DOT tonnage for the year, but is still a greater than 595 percent increase from the estimated 16.8 million tons in the 2009 construction season. WMA made up 31.2 percent of the total estimated asphalt mixture market in 2016. Production Plant foaming, representing nearly 77 percent of the market, is the most commonly used warm-mix technology; chemical additive technologies accounted for a little more than 21 percent of the market.”

Therefore, based on the above NAPA statement, that total WMA production was 116.8 million tons and that it represented 31.2 percent of the total estimated asphalt mixture market in 2016, one can estimate that ~375 million tons of asphalt mixture was produced in the U.S. in 2016. So, application of the same assumptions from the Missouri example (above) to 375 million tons of asphalt mixture produced nationwide would result in ~470,000 tons of resin required to meet the need nationwide.

Strictly for discussion purposes, let us assume BSA envisions 10 factories once production is at full-scale. That would be ~280,000 tons of resin produced annually by one company. Taking into account the PanAridus projection of 500,000 tons of resin produced annually (by all producers) if the U.S. natural rubber needs are met, it seems resin supplies would be more than adequate to meet demand from the paving industry, based on the example scenario.

As with many ideas and existing technologies, commercialization did not, necessarily, follow a straight line. Such is the case with the guayule plant. Serious efforts in commercialization over the last 100+ years have usually come as the result of a military, economic, or health crisis and once the crisis was over, interest declined [33]. Currently, interest is high because of concerns over the status and long-term stability of the natural rubber market [112]. Thus, guayule may finally be on the cusp of becoming an established source of high-quality natural rubber. If so, process by-products like the resins and bagasse will require further investigation to determine their potential as marketable co-products, i.e. by-products with value.

4.4. FUTURE RESEARCH

Follow-up research to this study is focused on an experimental paving project using the BSA and PanAridus crude resins. Approximately 11 tons of the BSA resin and 5 tons of the PanAridus resin are currently stored at Missouri S&T. Research proposals have been, or are in the process of being submitted for further laboratory verification of the use of the BSA and PanAridus resins as binder modifiers and a field demonstration using these resins in a paving project somewhere in Missouri.

APPENDIX A

MAJOR PROJECT COLLABORATORS AND EVENTS

The following discussion gives descriptions of the major collaborators and associated events that helped shape the journey over the last 12 years. The information is given in a manner that is as chronologically correct as possible to establish the general timeline but also retain brevity of presentation.

USDA-ARS and Yulex Corporation Era (2006-2014)

The initial contact with a “guayulero” (i.e. a guayule enthusiast [113]) was with Dr. Francis Nakayama in late-summer, 2006. In mid-2007, correspondence began with Dr. Colleen McMahan, a research chemist with the USDA Agricultural Research Service (USDA-ARS). Through Dr. McMahan, contact was established with Dr. Katrina Cornish in the summer of 2008.

Dr. Cornish was the Senior Vice President, Research and Development, of the Yulex Corporation. Dr. Cornish was considered the leading U.S. scientific expert on guayule cultivation and domestic production of hypoallergenic guayule latex for safe medical devices and specialty consumer products. She had previously worked at the USDA-ARS but joined Yulex in 2004. The list of her guayule-focused patents and publications is extensive. In May, 2009, she agreed to become a member of the NCHRP-IDEA expert panel for the project and was an invaluable source of knowledge and support. In 2010, Dr. Cornish became a professor and Ohio Research Scholar, Bioemergent Materials, at Ohio State University in Wooster, Ohio, but continued in her role as a member of the NCHRP-IDEA project expert panel.

Approximately a year after the NCHRP-IDEA project had started, contact was established with Dr. William W. Schloman, Jr., another guayulero with extensive experience working on guayule rubber and resin processing, and product development.

At the time of contact, he was retired from the University of Akron, Ohio. He had previously been a senior research chemist with Goodyear Tire and Rubber (1977-1983) and then a senior research scientist with Bridgestone/Firestone (1983-1990). His expertise in the chemistry of guayule rubber and resin was extremely helpful during the NCHRP-IDEA project. Additionally, his keen knowledge of the history behind the efforts to cultivate guayule in the U.S. was a highly-valued resource. His explanations of the various reasons why commercialization of the guayule plant has never quite materialized were informative and forthright [33].

Yulex supplied the majority of the guayule-based feedstock used during the NCHRP-IDEA project. Dr. Cornish, Jim Mitchell (Yulex VP of technology development), and Ray McCoy (Yulex pilot plant manager) delivered several different guayule-based materials over the course of the project:

- Approximately 1 ton of pelletized whole-shrub.
- Several hundred pounds of dried, post-latex-extraction (PLE) bagasse.
- Pelletized PLE bagasse.
- Whole and pelletized waste-stream leaves/stems.
- 10 gallons of latex (via Centrotrade Minerals and Metals).
- Dried latex.
- A sample of waxy, resinous material produced during an experimental supercritical fluid extraction run.

Dr. McMahan, David Nicholson (technology transfer coordinator, USDA-ARS), and Dr. Terry Coffelt (research geneticist, USDA-ARS-USALARC) delivered additional guayule-based materials, over time, from USDA-ARS research facilities:

- Three more gallons of the de-rubberized resin first submitted by Dr. Nakayama.
- Hundreds of pounds of chipped whole-shrub.
- Approximately 30 gallons of a rubbery, resinous precursor to the de-rubberized resin (in a 55 gallon drum labeled, “Resin, 8-24-90, #380”).

Bridgestone Americas and PanAridus Era (2013-Present)

Bridgestone Americas (BSA) is the U.S. subsidiary of Bridgestone Corporation, which has a long history in the rubber and tire industry [114]. The first contact with BSA was also made possible through Dr. Colleen McMahan. In May, 2013, Dr. McMahan indicated that the original sample of guayule rubber submitted by Dr. Nakayama in 2006, and the drum of rubbery, resinous precursor material had become “hot commodities.” She requested that the block of bulk rubber be sent to her at the USDA-ARS, and the drum of precursor material be sent to Dr. Yingyi Huang, a senior research engineer with BSA at their Akron, Ohio, research facility. Correspondence with Dr. Huang was necessary to accommodate the shipment of the precursor material to Akron, thus making her the first BSA contact.

An important and relevant event occurred on September 22, 2014: a ribbon cutting ceremony took place at the new BSA Biorubber Process Research Center in Mesa, Arizona [115]. This event is important because it denotes a major commitment by private industry to commercialize guayule rubber. It is relevant because, as will be discussed later, some of the personnel at the facility have become instrumental in the author’s endeavor.

In January, 2015, Mike Fraley, founder and CEO of PanAridus, LLC, contacted the author after reading the ASCE paper based on the NCHRP-IDEA project final report. PanAridus, founded in 2009, is an Arizona-based biotechnology company specializing in genetics, yield optimization, agronomics, and rubber extraction processes required to commercialize guayule. PanAridus was involved in the Biomass Research and Development Initiative (BRDI) grant, “Securing the Future of Natural Rubber—an American Tire and Bioenergy Platform from Guayule.” The grant was a 5-year, $6.9 million research project that began in 2012 and was funded by the Department of Energy and the USDA. PanAridus was part of a research consortium during that project that included Cooper Tire and Rubber Company (the lead entity), Clemson University, Cornell University, and the USDA-ARS [116].

Through Dr. Yingyi Huang of BSA, contact was established in March, 2015, with Dr. Michael Beaulieu, senior materials scientist, also at the BSA research facility in Akron, Ohio. Extensive interaction with Dr. Beaulieu resulted in the receipt of four different guayule-based materials in two different shipments. The first shipment arrived March 9, 2016 and contained several quart cans of the raw resin by-product of rubber extraction at the BSA Biorubber Process Research Center in Mesa, Arizona, and a multi-pound block of the raw resin that had been processed to remove most of the lighter, more volatile fractions. The second shipment arrived on June 14, 2016, and contained a small sample (200 grams) of the devolatilized resin with a moderate amount of residual rubber, and another similarly-sized sample of devolatilized resin with a larger amount of residual rubber. Laboratory evaluations were performed on the raw resin (still containing volatiles), the devolatilized raw resin, and the devolatilized resin with a moderate rubber content. The results were sent to Dr. Beaulieu as they became available.

In May of 2015, just a few months after the initial contact with Mike Fraley, Dr. Bruce King, senior polymer researcher for PanAridus, contacted the author. Discussions focused on the resin PanAridus was generating at the time, and future plans to work together to promote its use in FPMs. Within three weeks of the initial contact with Dr. King, the first delivery of PanAridus resin occurred. The first sample was about two gallons of their latest process run or crude resin. Upon initial inspection, the PanAridus resin had similar viscosity, color, and odor as the original USDA-ARS de-rubberized resin sent by Dr. Nakayama in 2006. This was very encouraging. However, this first batch of resin was different from the USDA-ARS resin in that it contained a considerable amount of low molecular weight rubber that would float to the top of the sample if left undisturbed for a sufficient amount of time. Laboratory evaluations of the more resinous portion of this sample were performed and the results were reported to Dr. King and Mike Fraley.

Since the beginning of the relationship with PanAridus, four separate deliveries of their resin to the Missouri S&T asphalt laboratory have occurred: the first arrived May 29, 2015 (described above), the second on February 16, 2016, and the third on July 12, 2016. The second sample had been some of the process run resin improved (refined) in the laboratory by removing more of the low molecular weight rubber and solvents (hexane and acetone), and the third sample was a newer process run resin based on those improvements. The last delivery, March, 2017, was approximately 5 tons (20, 55-gallon drums) of resin that the company had collected and stored since startup of their processing facility. The intent is to use this resin in an experimental paving project, to be discussed later in this document.

At the invitation of Dr. Cornish, the author gave a presentation at the October, 2015, 27th annual meeting of the Association for the Advancement of Industrial Crops (AAIC) on the work accomplished during the NCHRP-IDEA project, and the preliminary testing of the original sample of PanAridus resin. At that meeting, Dr. Colleen McMahan and Dr. William Schloman were in attendance and the first face-to-face discussions with them took place with much pleasure and gratitude. Also in attendance were Dr. David Dierig, section manager of agricultural operations at BSA, and Dr. Lauren Johnson, agricultural research director with PanAridus. On a side note, it was during this same month that Bridgestone announced it had successfully built tires in which 100% of the natural rubber components were derived from the guayule plant.

Through Dr. Dierig, contact was established with William Niaura, director of new business development, and Bob White, section manager of research at the BSA Biorubber Process Research Center. Through William Niaura and Bob White, approximately 11 tons (60, 55-gallon drums) of the BSA resin were delivered to Missouri S&T on September 21, 2016. This resin and the 5 tons of PanAridus resin are intended to be used on an experimental paving project.

Continuing Contact and Recent Activities

Correspondence has continued with many of the major players described above: Dr. Inam Jawed, Dr. Colleen McMahan, Dr. Katrina Cornish (whom the author finally met in person in 2017 at the 29th Annual AAIC meeting in Ames, Iowa), Jim Mitchell, Dr. William Schloman, Mike Fraley, Dr. David Dierig, William Niaura, and Bob White.

A few new contacts have been made very recently: Dr. Howard Colvin, a senior scientist at Cooper Tire and Rubber Company, and Dr. Everett Crews, technology development director for Ingevity (a specialty chemical company that develops and markets binder modifiers).

One of the most informative and enjoyable recent activities was a tour of the BSA Biorubber Process Center in Mesa, Arizona, on February 6, 2018 [117]. Bob White arranged for the author to tour the center and discuss the potential of any follow-up research. It was during this same week that the author attended the Association for Modified Asphalt Producers (AMAP) conference in Phoenix, Arizona, and established contact with Dr. Everett Crews, the president of AMAP.

Because the fondness for the inconspicuous guayule plant continues to grow, it should be noted that several research proposals have recently been submitted.

An equipment grant proposal submitted in August of 2016 was awarded in June of 2017. The funding agency was the USDA, National Institute of Food and Agriculture, Agriculture and Food Research Initiative (USDA-NIFA-AFRI), Sustainable Bioenergy and Bioproducts Challenge Area program. The grant was for a $63,000 asphalt testing system that affords several methods of evaluating the fatigue and thermal cracking potential of FPMs. This may strike one as confusing or unusual. However, the proposal was written in a way that 1) stressed the necessity of obtaining the system to continue pursuing the use of guayule resin in FPMs, and 2) made the case the system would add to the educational opportunities at Missouri S&T. The device is capable of performing the Disk-shaped Compact Tension (DCT) test (a cold-temperature or thermal cracking test), and the Semi-Circular Bend (SCB) test (a room-temperature fatigue cracking test). Figure A1 shows the DCT/SCB device and specimen preparation equipment.

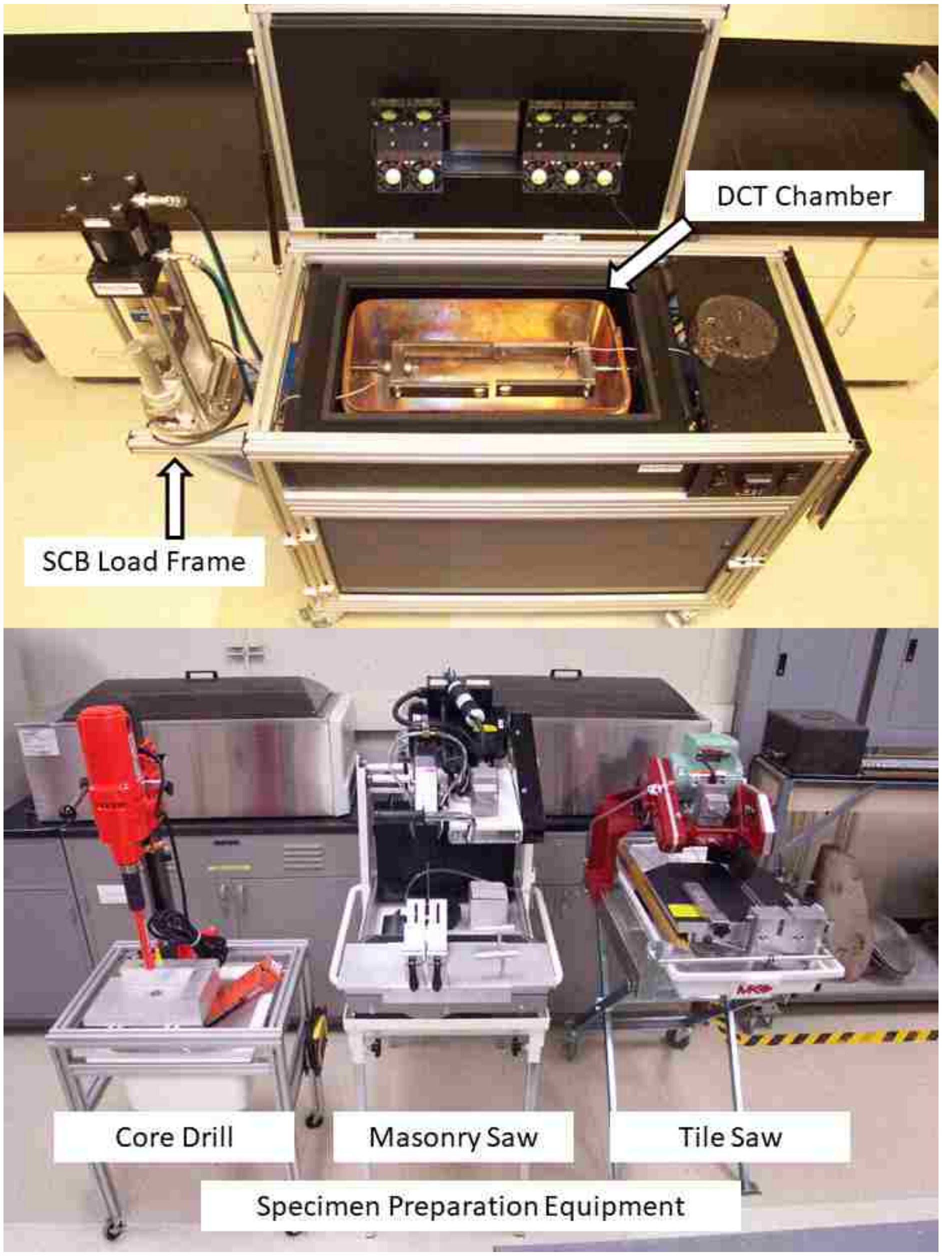


Figure A1. DCT/SCB Device and Specimen Preparation Equipment

The USDA funding agency covered 50% of the total cost and the remaining 50% was picked up by several entities on the Missouri S&T campus: the Office of Sponsored Programs (OSP), the Department of Civil, Architectural, and Environmental Engineering (CArEE), and the Center for Infrastructure Engineering Studies (CIES). Noteworthy is the fact that through the proposal/award process, contact was established with Dr. William Goldner (National Program Leader, Biomass Feedstock Development and Production Systems, Division of Sustainable Bioenergy, Institute of Bioenergy, Climate, and Environment), and Dr. Toby Ahrens (National Program Leader, Agricultural Bioproducts), both with the USDA-NIFA program. Additionally, these two officials were very familiar with the BSA Biorubber Process Center.

A NCHRP-IDEA Type 2 (transfer to practice) proposal was submitted in March, 2017. The focus of the proposed research was to validate the BSA and PanAridus resins for use as binder modifiers, and to perform an experimental paving project in Missouri. That submittal and a subsequent re-submittal in August of 2017 were declined funding. However, Dr. Inam Jawed indicated that another re-submittal would not be discouraged. With input, again, from Dr. Toby Ahrens at the USDA-NIFA offices, a Letter of Intent (LOI) to submit an Exploratory Research proposal was sent on February 3, 2018 to the USDA-NIFA-AFRI, Foundational Program. The proposed work was along the very same lines as the NCHRP-IDEA Type 2 proposal. On February 13, 2018, a response from the LOI reviewers indicated that they would not discourage submission of a full proposal, but they thought the proposed work did not meet the Exploratory Research program criteria and there were other, more appropriate programs within the Foundational Program catalog.

On February 11, 2018, a research idea (i.e. a brief summary of the NCHRP-IDEA Type 2 proposal) was submitted to the Transportation and Environmental Research Ideas (TERI) database, maintained by The Center for Environmental Excellence within the American Association of Highway and Transportation Officials (AASHTO) organization. AASHTO's Committee on the Environment and Sustainability regularly reviews the ideas for merit and then makes them available to policy makers and researchers that have access to the database.

It is the intent of the author to submit another proposal, based on the NCHRP-IDEA Type 2 proposal, through the USDA-NIFA-AFRI Foundational Program. The applicable research area within the Foundational Program to which the proposal will be submitted is called Bioprocessing and Bioengineering. The description of this area of research does seem much more appropriate for the author’s intended research than the Exploratory Research area, to which a LOI was earlier submitted, and softly discouraged.

APPENDIX B

ACETONE-EXTRACTION AND RECOVERY OF GUAYULE RESINS

As described in the Laboratory Investigation section, 11 different combinations of guayule feedstock, solvent(s), and extraction/recovery procedures were ultimately performed and the resultant extracts evaluated for use as a recycling agent. A few of the simpler and more complex procedures were described in the Laboratory Investigation section: visual observations of some of the acetone-extracted materials, pentane-aqueous methanol liquid-liquid extraction, and cold-filtered ethanol-partitioning. However, the majority of the extractions and recovery procedures involved one feedstock and one solvent; e.g. pulverized whole-shrub and acetone.

There are two sections in this Appendix: a section describing a basic procedure for acetone-extraction and recovery of the whole-shrub resin, and a section describing a procedure for the acetone-extraction and recovery of the RR from the dried latex.

Acetone-extraction and Recovery of Pulverized Whole-shrub Guayule Resin

The chipped guayule shrub (particles pass a 3/8 inch opening; i.e. -3/8 inch) was further reduced in size (-1/16 inch) by pulverizing using a horizontal shaft impactor. Five kilograms of the pulverized shrub was dried in a 60°C, forced-air oven for 24 hours (see Figure B1). The drying step was not performed to determine moisture content but to remove most of the moisture so it did not show up in the resin (if possible) or in the recovered acetone.

The dried, pulverized shrub was soaked in 11 liters of ACS certified acetone for 24 hours, at room temperature, with occasional stirring. The resin-acetone solution (miscella) was drained and filtered (~75 micron mesh filter), and stored in glass containers. A second 24 hour soaking of the shrub in 7 liters of fresh ACS certified acetone was performed. The miscella from the second soaking was also drained and filtered, and stored in glass containers.

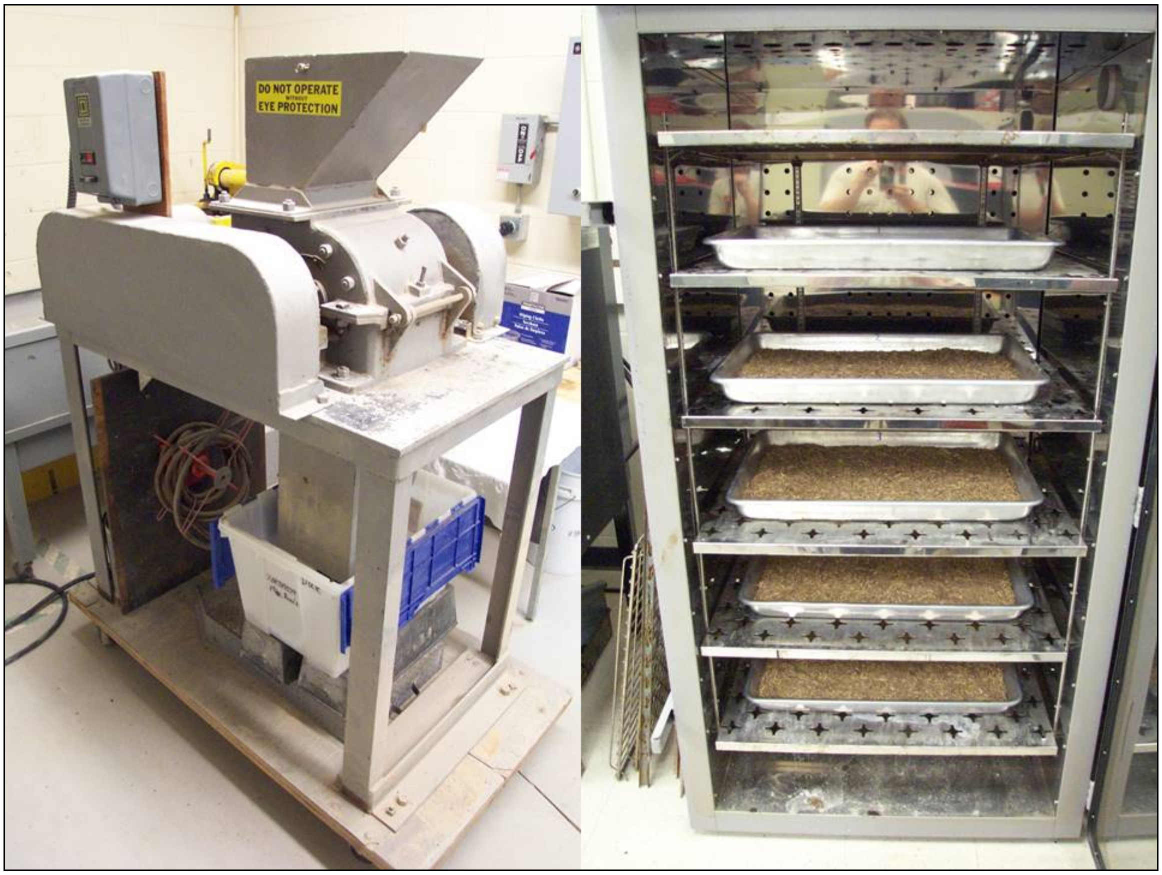


Figure B1. Horizontal Shaft Impactor and Drying Ovens

The majority of the adsorbed/absorbed miscella remaining in the bagasse was then removed using a bowl-type batch centrifuge as described in the binder extraction procedure, AASHTO T 164 Method A [75]. All collected miscella was further clarified (i.e. fines removal) using a large centrifuge described in the binder recovery procedure, AASHTO T 170 [70]. Figure B2 shows the various steps just described.

A solvent-resistant plastic bag, supplied with the 20-liter solvent recovery device (SRD), was placed in the SRD to facilitate easy removal of the SRD residue. The clarified miscella was placed in the SRD bag, the SRD lid was secured, and the program was initiated to begin primary distillation. Figure B3 shows the loaded SRD.

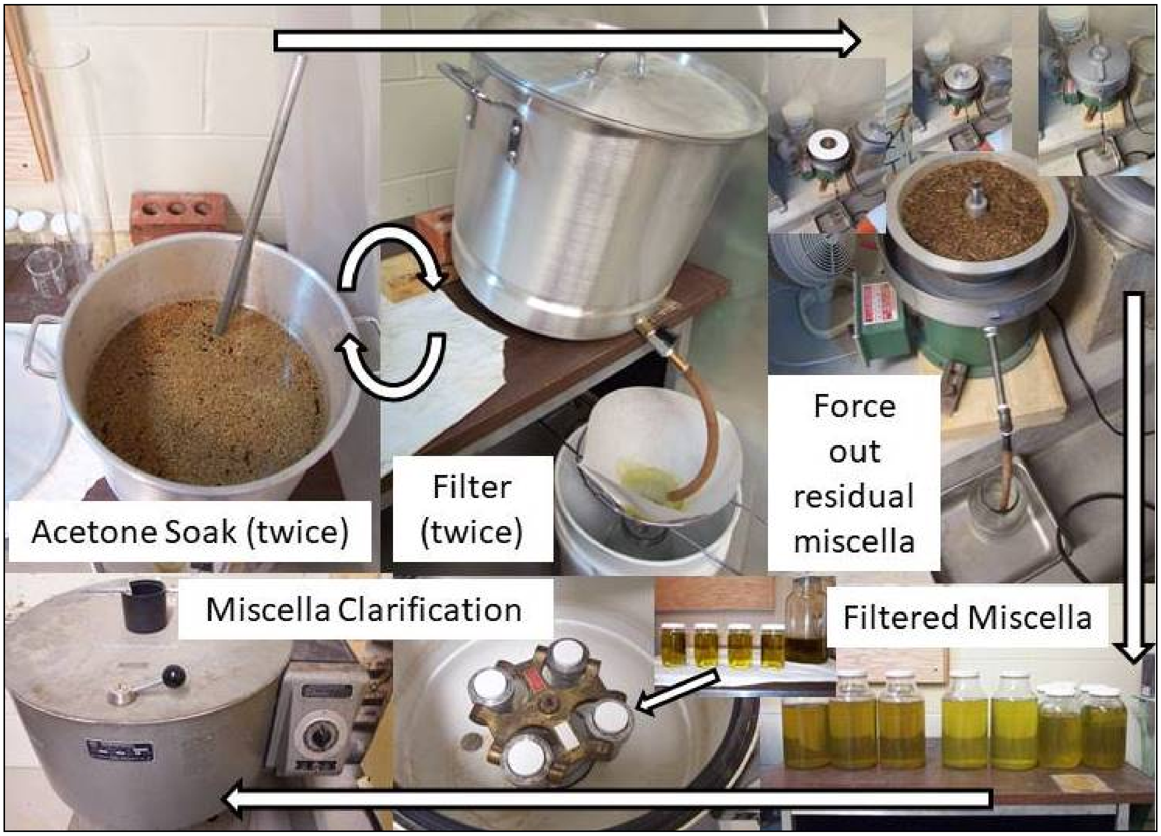


Figure B2. Extraction of Whole-shrub Resin

The SRD is programmable with the capability to run two different cycles of heating time and temperature, which allows for a double boiling point distillation (i.e. a two solvent mixture), if necessary. For primary distillation of the miscella, the first cycle was set to run for 8 hours with the oil-bath heating temperature set at 88°C. The second cycle began immediately following the end of the first cycle and ran for one hour at

78°C. The lower temperature setting during the second cycle is an attempt to maximize the acetone removal yet minimize thermal damage to the resin. Although the SRD manual specifically states that the second cycle heating temperature must be greater than the first cycle temperature, the manufacturer was contacted and, after some testing, indicated that the second cycle temperature could be up to 15° lower than the first cycle temperature without a programming error.

Figure B3. Guayule Resin-Acetone Miscella in the SRD

Once the primary distillation program ended, the SRD was allowed to cool for several hours. Once cool, the SRD bag containing the resin (and a small amount of acetone) was removed and drained into a glass container. Figure B4 shows the primary distillation product in a quart (~1 liter) jar.

It is notable that approximately 17 liters of miscella were introduced into the SRD for primary distillation. About one liter of acetone was lost in the process, left in the bagasse and lost to evaporation. The use of the SRD, which ran unattended for about 11 hours (overnight), made the primary distillation procedure extremely simple and efficient, reducing the miscella from 17 liters to about one-half liter.

Figure B4. Primary Distillation Product

Final distillation of the miscella during the trial batches was performed using the rotary evaporator device. The initial specimen mass was approximately one hundred and fifty (150) grams, about one-third (1/3) of the SRD product shown in Figure B4. Test methods referenced for performing final distillation were AASHTO T 319 [76] and ASTM D 5404 [77]. Because these methods are applicable to asphalt binder, several deviations from the standard procedures were imposed because of the natures of the solvent and the extractive, i.e. acetone and guayule resin, respectively. For example, the hot oil bath temperature for resin recovery was set at 70°C (acetone's boiling point is 56°C at atmospheric pressure) whereas specified oil bath temperatures for binder recovery are higher: 100°C and 174°C for AASHTO T 319, and 140°C for ASTM D 5404. The level and sequencing of the applied vacuum, the flask rotation rate, and the nitrogen gas purge rate during resin recovery also deviated from the AASHTO and ASTM specifications.

For batches #11 and #12 (the two acetone-extracted whole-shrub resin batches used for the binder blending mixture experiment), final distillation proceeded as follows:

1. The SRD (primary distillation) product was divided into thirds with each third placed in a 2000 ml boiling flask.
2. The hot oil bath set point temperature was increased to 110°C in an attempt to remove any residual water and to decrease resin viscosity thereby increasing the potential for maximum acetone removal. However, the temperature was not set so high as to drive off potentially beneficial compounds.
3. The condenser chiller set point temperature was 20°C. It has been observed that the rotary evaporator condenser temperature needs to correlate to the boiling point temperature of the solvent in order to optimize solvent removal; i.e. if the condenser is too cold, the solvent vapor condenses before reaching the condenser coil and returns to the boiling flask, while if the condenser is too hot, the solvent vapor bypasses the condenser coil and can accumulate in the vacuum pump oil.

4. The flask was rotated at 50 rpm while being lowered into the hot oil bath to its maximum possible depth; i.e. the flask was submerged in the oil to a depth of 1 – 2 inches.
5. Ten inches Hg gauge vacuum was applied, the nitrogen gas purge rate was set at ~200 ml/min, and flask rotation rate continued at 50 rpm for 5 minutes. Most of the acetone had been removed by the end of this time period.
6. Flask rotation was stopped for a few seconds to allow the extractive to flow to the lowest point in the boiling flask and remix.
7. Flask rotation was resumed at varying lower rpm rates (e.g. 30 or 20 rpm) for varying amounts of time per rpm rate (e.g. 3 minutes @ 30 rpm and 2 minutes @ 20 rpm) for a total of 5 minutes. Rotation rate is based on the behavior of the extractive inside the boiling flask; it is desired that the extractive flow down the upwardly moving side of the boiling flask thus shearing the extractive and exposing the trapped acetone. Experience plays a big part in determining rotation rate.
8. Rotation rate was increased (e.g. 40 rpm) then the vacuum level was increased to 15 inches Hg gauge vacuum. The nitrogen purge was allowed to increase on its own as a result of the increased vacuum. Flask rotation was again varied and intermittently stopped. This step continued for ~5 minutes.
9. The vacuum was incrementally increased over a period of another ~5 minutes to a maximum of 20 inches Hg gauge vacuum where the nitrogen purge rate was held at ~1000 ml/min. The vacuum and nitrogen purge rate were held at these levels for 30 minutes while the flask rotation was varied and intermittently stopped to maximize acetone removal.

10. After a total of ~50 minutes of final distillation, the vacuum was released, the nitrogen purge and flask rotation were stopped, and the flask was raised from the hot oil bath to allow the excess oil to drip back into the bath. The remaining oil was wiped from the flask with clean rags, and the flask was weighed to determine the amount of binder recovered.
11. The flask was put into a 145°C oven and allowed to sit with the neck oriented horizontally for 10 minutes to allow the majority of the extractive to flow to one side of the flask. After 10 minutes, the flask was inverted and allowed to flow into a storage container (a one quart, unlined paint can) for an additional 15 minutes. The emptied flask was then weighed to determine the binder content remaining in the flask.

Steps 2 through 11 were repeated for the remaining 2 boiling flasks with all of the recovered resin accumulated in the same one quart paint can. Figure B5 shows the rotary evaporator station, a sample being desolventized, and drainage of the boiling flask.

The same basic, scaled-up procedure outlined above was used for the hexane extraction and recovery of the LF material, as well. Details such as SRD temperature settings, rotary evaporator operations, etc. were different due to the nature of the solvent and the resultant extract.

Acetone-extraction of the Dried Latex RR

Yulex supplied about 50 pounds of the dried latex rubber over the course of several months during 2011-2012. As with many of the procedures developed during this study, extraction of the RR from the dried latex evolved over time. The major difference between extraction/recovery of the RR from the dried latex and the extraction/recovery of the resin from the whole-shrub (described in the previous section) was in how the dried latex rubber was handled prior to introducing the resin-acetone miscella into the SRD. Details are given below.

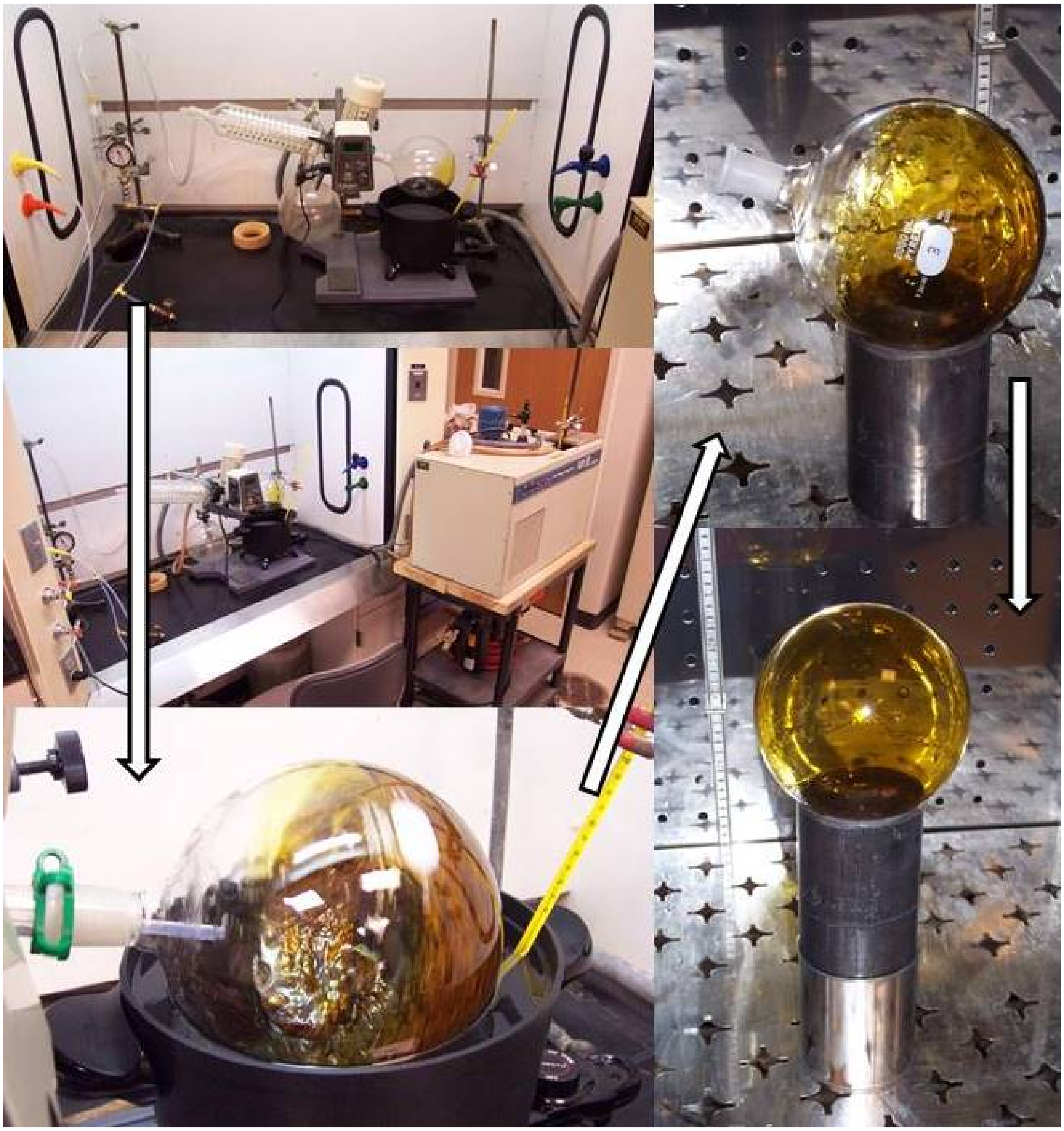


Figure B5. Final Distillation - Resin Recovery Procedure

The first major hurdle to overcome was how to reduce the dried latex rubber samples supplied by Yulex to a size that would maximize RR yield; i.e. the surface area of the rubber to be exposed to acetone needed to be maximized. Figure B6 shows what the rubber samples looked like upon arrival.

Figure B6. Dried Latex Rubber Sample as Delivered

The rubber sample was a long tube of dried latex that had been wrapped into a round shape or plug. Processing of the plugs to prepare for the acetone-soak changed over time. When the first sample arrived, the initial step in sample preparation was to "uncoil" the tube by starting at the exposed end of the tube and cutting it away from the main body of the plug with a box cutter, as best as possible. The rubber "rope" was then cut into smaller pieces using scissors. Figure B7 shows the end result of this early method of size reduction.

Figure B7. Earliest Method of Rubber Plug Size Reduction

It became apparent, pretty quickly, that the size reduction method needed some modifications. It was well known that the scrap tire industry used two methods for production of ground tire rubber: 1) shearing the scrap rubber at ambient temperature (basically the method shown in Figure B7), and 2) freezing/hardening the scrap rubber with liquid nitrogen and fracturing through impact. Freezing and fracturing of the dried latex rubber was adopted for this study and became instrumental in speeding up the process of RR extraction and recovery.

An additional method of speeding up the process was to use a band saw to reduce the plugs to a size that could be frozen with liquid nitrogen and then dropped into the pulverizer for flaking. Figure B8 shows the process that was used for the majority of the RR extraction and recovery activities. Explanations of the numbered steps are given below Figure B8.

Figure B8. Basic Procedure for RR Extraction and Recovery

1. The dried latex rubber plug, as delivered.
2. The rubber plug was cut into ~2 inch cubes using a band saw.
3. Immersion of several cubes of rubber into liquid nitrogen for several minutes to allow for thorough freezing/hardening of the rubber.
4. The frozen cubes were immediately dropped into the pulverizer.
5. The rubber was flaked and captured in a receptacle underneath the pulverizer.

6. The flaked rubber was immediately submerged in acetone, covered, and allowed to soak at room temperature for a certain amount of time (usually 24 hours).
7. Primary distillation of the resin-acetone miscella proceeded in the SRD as was described in the previous section.
8. Final distillation of the SRD residue proceeded in the rotary evaporator as was described in the previous section.

Beginning with the fifth batch of RR extracted and recovered, the flaked rubber was submerged in acetone on a double-stack of screens, inside a home-made pressure vessel; a 30-gallon drum outfitted with compressed air connectors, regulator, and pressure gauge. Pressure during soaking was kept low, approximately 5 psi.

The purpose of the pressurized acetone-soak was to increase the yield of the RR in hopes to not only increase the amount of RR on hand for laboratory testing but to demonstrate to Yulex that the rubber could be made whiter (one of Yulex's initial goals when the acetone-extraction of the RR was first suggested). Figure B9 shows the pressure vessel setup. Explanations of the numbered steps are given below.

1. View of the home-made pressure vessel. The lid had a rubber gasket to give a tight fit on the drum rim, and the lid openings were welded and silicone-caulked on the underside to prevent any leaks during pressurization. The all-thread was attached to a large aluminum plate on which the drum sat.

2. View of the first layer of flaked rubber suspended off of the bottom of the drum on a piece of window screen. The second layer of window screen is in place on top of the first layer of rubber.

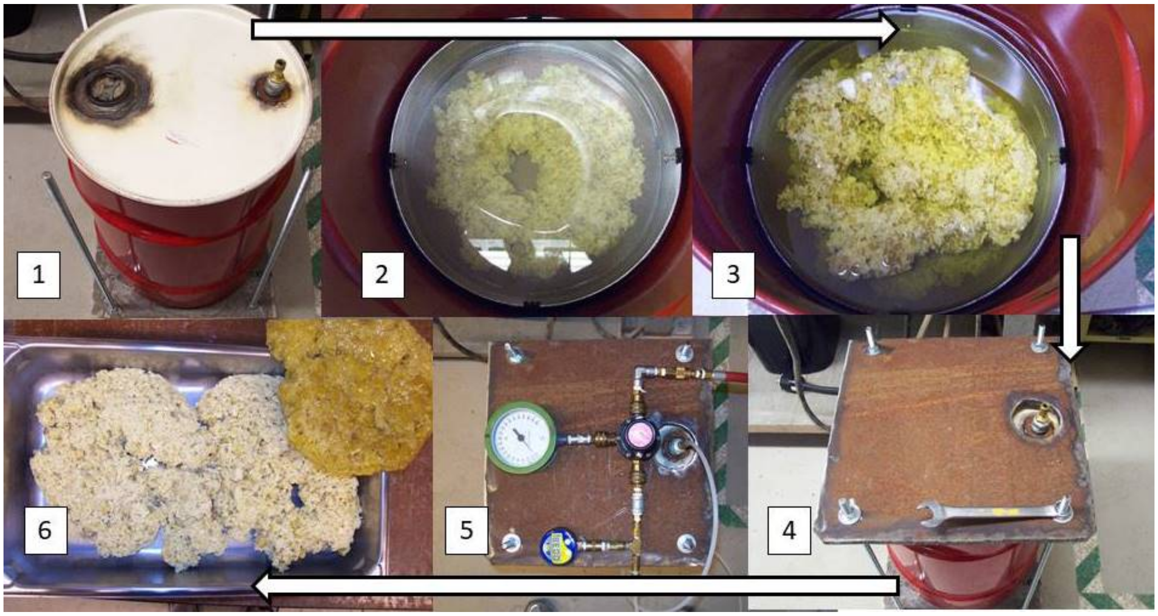


Figure B9. Pressure Vessel Setup for Acetone-Soaking Under Pressure

3. View of the fully-loaded drum with two layers of flaked rubber suspended on window screen inside of the drum.
4. Securing of a heavy steel plate on top of the lid to keep the pressure seal tight.
5. Pressure regulator and applied pressure gauge configuration.
6. Visualization of the difference in color of the rubber after RR extraction under pressure (two whiter pieces, bottom left) and without pressure (amber-colored piece, top right).

The color differentiation in the two samples of deresinated rubber shown in Figure B9 is dramatic but it should be noted that the whiter pieces were still wet with acetone. After some time, the whiter pieces would dry and darken somewhat, but not to the degree of the more amber-colored piece in the image.

The effect of the pressurized acetone-soak can be seen in the yield results in Table 3.3 in the Laboratory Investigation section. The first four batches, those soaked in acetone at atmospheric pressure, yielded 11.9% RR, on average. The last four batches, those pressurized during acetone-soaking, yielded an average of 14.0% RR, an increase in yield of about 17%.

There were a total of 14 different extraction and recovery runs performed to obtain the RR needed for the project. Not all of the runs, however, were performed in such a manner as to obtain statistical data. Some were performed as part of the learning process and others, specifically at the end of the study, were performed simply to obtain enough RR to complete the laboratory investigation.

APPENDIX C

EXTRACTION AND RECOVERY OF RAP AND RAS BINDERS

RAP Binder Extraction/Recovery

Based on the previously determined binder contents of the two RAPs utilized in this study, ~5.0% for RAP1 (from a Missouri Department of Transportation roadway) and ~5.5% for RAP2 (from a municipal street), specimen size was held to ~10 kg of RAP per batch in order that the primary and final distillation equipment would not be overloaded with solvent (trichloroethylene or TCE) and/or recovered binder.

RAP Binder Extraction

The basic steps of the RAP binder extraction procedure were as follows:

1. Five pans, each containing ~2 kg of RAP, were first weighed then put in a 60°C oven overnight (≥16 hours).
2. The following morning, Pan #1 was removed from the oven, quickly weighed, and 1200 ml of fresh, technical grade TCE was placed in the pan with the warm RAP.
3. The RAP in Pan #1 was stirred, covered, allowed to sit for 5 minutes, stirred one more time, and then allowed to sit undisturbed for 10 minutes of soaking.
4. Moving slowly so as not to re-suspend the settled fines, the majority of the binder/TCE solution in Pan #1 was decanted through a deep-fat fryer filter funnel (~75 µm mesh) and into a 2 liter glass jar, while being careful not to spill or lose any RAP aggregate (the pan angle rarely exceeded 45°).
5. An additional 100 ml of fresh TCE was added to Pan #1, and then the pan was swirled in a circular motion while held at a slightly-inclined angle in order to move the aggregate to the drip-free, pouring corner of the pan. The pan was propped up at this angle and allowed to sit undisturbed for 2 – 3 minutes.

6. The binder/TCE solution was, again, decanted through the filter funnel into the 2 liter glass jar.
7. Using a stainless steel spoon, the RAP aggregate remaining in Pan #1 was carefully transferred to a one gallon, unlined paint can. Pan #1 was then rinsed with the minimal amount of fresh TCE into the gallon can.
8. A lid was placed loosely onto the gallon paint can and Can #1 was placed into an 80°C oven. 80°C was chosen because it is hot enough to re-warm the RAP aggregate but does not exceed the boiling point of TCE, 86°C.
9. The filter funnel was rinsed with fresh TCE, and then set aside for 2 more uses. A new filter funnel was used for Pans #4 and #5. The 2 liter glass jar of binder/TCE solution was lidded and set in a safe place.
10. Steps 2 – 9 were repeated for Pans #2 through #5. There were now 5, one gallon cans of RAP aggregate and TCE in the 80°C oven.
11. One to two hours later, the warmed Can #1 was removed from the oven, 700 ml of fresh, technical grade TCE was added to the can, the lid was securely attached with a hammer, and the can was placed on its side inside the drum of a wet-ball mill device (see Figure C1). This particular step was included to approximate guidance in AASHTO T 319 [76] in which a specified extraction vessel is rotated at a specific rpm for a specific length of time, the purpose being to maximize the separation of bound aggregate particles in the RAP and, thus, maximize binder extraction
12. Can #1 was rotated at 60 rpm for 5 minutes in the wet-ball mill device.
13. After the 300 revolutions, the contents of Can #1 were transferred to a round, stainless steel pan, and then Can #1 was rinsed clean with fresh TCE.

14. The contents in the round, stainless steel pan were carefully transferred to the small centrifuge bowl specified in AASHTO T 164 [75], and the pan was rinsed with fresh TCE.
15. The contents in the centrifuge bowl were stirred slowly to distribute the solids evenly in order to minimize vibration during the high-speed rotation of the small centrifuge.
16. The centrifuge bowl was placed on the centrifuge, an oven-dry, pre-weighed filter ring (~4 µm mesh) was placed on the bowl, the lid was attached, and the binder/TCE solution was carefully centrifuged into a 2.5 liter glass jar.

Figure C1. Wet-Ball Mill Device Used For Can Rotation

17. Three subsequent washes of the RAP aggregate in the centrifuge bowl were performed using 200 ml per wash of TCE recovered during the previous batch extraction (i.e. the TCE had only been used once before).
18. The RAP aggregate was removed from the centrifuge bowl, put back into the round, stainless steel pan and put into a 105°C drying oven, along with the filter ring. The

filter ring before-and-after weights were used to determine the amount of fines (≥ 4 μm) captured by the filter ring.

19. The 2.5 liter glass jar was lidded and set aside in a safe place.
20. Steps 11 – 19 were repeated for Cans #2 through #5.

RAP Binder Recovery

The basic steps of the RAP binder recovery (i.e. primary and final distillation) were as follows:

Primary distillation:

1. The 2 and 2.5 liter glass jars were allowed to sit undisturbed for at least 4 hours to facilitate settlement of the considerable fines still present, especially in the 2 liter glass jars containing the first-soak binder/TCE solution.
2. After considerable settling time, the SRD was loaded with a bag, and all 10 glass jars were slowly poured into the SRD bag, attempting to keep as many fines in each jar as possible.
3. After each jar was poured into the SRD bag, fresh and/or recovered TCE was used to rinse the residual contents of the jar into a pre-weighed "fines" jar. The idea was to continually isolate fines through a series of settlement periods to minimize the amount of fines in the binder/TCE solution during the upcoming large centrifuge procedure.
4. The SRD was programmed to run at 115°C for 6 hours and was then turned on.
5. The following morning, after checking to make sure the SRD had cooled to a safe temperature, the small amount of binder/TCE solution in the "fines" jar (~500 ml)

was slowly decanted into the SRD bag that contained the primary distillation product. The “fines” jar was put into a 105°C drying oven for a “fines” (≤ 75 µm) weight determination at a later date.

6. The binder/TCE solution in the SRD bag was transferred to a rectangular, stainless steel pan with a drip-free pouring corner.
7. Using a glass funnel, the binder/TCE solution was then transferred in approximately equal parts to 8, 250 ml plastic centrifuge bottles. The pan was rinsed with TCE and the rinse solution was used to equalize the level of binder/TCE solution in the 8 bottles such that their weights would be approximately equal.
8. The 4-cup centrifuge rotor had to be balanced so each pair of opposing filled centrifuge bottles and their corresponding centrifuge rotor cups were balanced by weight using a glass pipette to transfer solution from the heavy bottle/cup to the light bottle/cup.
9. The large, now balanced, centrifuge was run for 45 minutes at an rpm rate that resulted in a force of at least 770 times the force of gravity on the binder/TCE solution.
10. The contents of 2 of the centrifuge bottles were transferred to a 2000 ml boiling flask for final distillation. A total of 4 boiling flasks were used for final distillation of each batch of RAP (and RAS).

Final distillation:

The final distillation procedure basically followed the steps outlined in the Acetone-Extracted Whole-Shrub Resin Extraction/Recovery section above, except for the following major items:

1. The hot oil bath temperature was set at 175°C.
2. The condenser chiller temperature was set at 30°C.
3. The initial flask rotation rate was 60 rpm.
4. The flask was initially lowered into the hot oil bath such that the flask barely came into contact with the oil. This was done to reduce the initial condensation rate to a safe level. Once the majority of the TCE had been removed from the boiling flask, the flask was then lowered into the oil to its maximum depth (1 – 2 inches).
5. The initial vacuum level was set to ~5 inches Hg gauge vacuum.
6. Carbon dioxide was used instead of nitrogen for the gas purge.

Vacuum and gas purge levels were incrementally increased, while flask rotation rates were varied and stopped intermittently, but in accordance with the behavior of the RAP binder in the flask and the condensation rate.

7. The maximum vacuum capable of being applied by the stand-alone vacuum pump was utilized. Once the vacuum had reached a level of 60 mm Hg absolute vacuum (~27 inches Hg gauge vacuum), final distillation was continued for another 30 minutes. During these 30 minutes, the vacuum increased slightly and generally ended up between 50 and 40 mm Hg absolute. During the highest vacuum application, the CO_2 gas purge rate could not be held below ~1200 ml/min without the flow rate indicator bead violently oscillating up and down the tube.
8. The oven temperature setting for draining the binder from the boiling flasks was 175°C.

Reclaimed Asphalt Shingle (RAS) Binder Extraction/Recovery

Because of the earlier determined RAS binder content of ~22%, original specimen size per batch was limited to ~2 kg (5 pans of 400 grams each). The basic procedure for extraction/recovery of the RAS binder was very much the same as outlined in the RAP binder extraction/recovery procedure above. The few exceptions are as follows:

1. Considerably less TCE was used during extraction because of the smaller specimen size per batch.
2. Due to the smaller amount of TCE, the SRD was programmed to run for 5.5 hours instead of 6.
3. The hot oil bath temperature setting during final distillation was 195°C.
4. The initial flask rotation rate was 80 rpm.

Once again, vacuum and gas purge levels were incrementally increased, while flask rotation rates were varied and stopped intermittently, but in accordance with the behavior of the RAP binder in the flask and the condensation rate. The RAS binder behaved much differently than the RAP binder once most of the TCE had been removed (usually within the first 5 – 10 minutes). The RAS binder "puffed up" and looked very much like a sponge in the flask, especially when the first increment of vacuum increase was applied.

5. Once the vacuum had reached a level of 60 mm Hg absolute vacuum, final distillation was continued for another 45 minutes. Because the viscosity of the RAS binder is so much higher than the RAP binder, the flask rotation was stopped most of the time during the last 45 minutes and when it was rotating, the rpm rate was set as low as the device would allow, ~8 rpm.

The oven temperature setting for draining the binder from the boiling flasks was 225°C and the time in the oven was 20 minutes horizontally oriented and 20 minutes inverted in the storage container.

APPENDIX D

BINDER-BLENDING PROCEDURE

The method for blending the different components involved using a Brookfield rotational viscometer (see Figure D1). Originally, the intent was to mix each blend at the same temperature. D'Angelo and Dongre performed research on polymer-modified binders and mixed all of the blends at 188°C for two hours using a high shear mixer, then stored the blends in a 163°C oven overnight [118]. Because the viscosities of the blends in this experiment could vary so widely, a different approach was adopted.

The Asphalt Institute published literature in which they present recommended mixing and compaction viscosities for HMA. The recommended binder viscosity for HMA mixing is 0.17 ± 0.02 Pa·sec or 170 ± 20 centipoise [90]. It seemed that mixing the blends at this viscosity for a short, but specific length of time would be the most logical method to use for several reasons:

- The binder materials would be very fluid at this viscosity and the potential for a more complete blending would be increased, relative to holding the mixing temperature constant, thus minimizing the potential for increased variability in the test results.
- Although the mixing temperatures for each blend will very likely be different, one could say that holding constant the viscosity during mixing across all blends would remove it as a variable in the binder-blending mixture experiment.
- The blending could take place over a short period of time (relative to the D'Angelo and Dongre method) thereby reducing the potential for excessive, additional hardening of the blended binders.
- The determination of the mixing temperature for each blend could be beneficial in the design and creation of FPMs.

Figure D1. Binder-Blending Mixer Using a Brookfield Rotational Viscometer

Using the rotational viscometer as a binder mixer posed an apparent problem in that the mixer impeller did not possess a standard geometry; i.e. the viscosity readings of the viscometer were not calibrated to the non-standard geometry of the mixer impeller and were, therefore, invalid. The problem was solved by observing the torque being measured by the viscometer at a particular revolutions-per-minute (RPM) rate while the mixer impeller was rotating within 150 grams of mineral oil at a viscosity of 170 centipoise. The temperature at which this particular mineral oil's viscosity was 170 centipoise (33.7°C) was previously determined using a second Brookfield viscometer setup strictly for viscosity testing. The viscometer in Figure D1 indicates 67.6% torque at

250 RPMs when the material within which the mixer impeller was rotating possesses a viscosity of 170 centipoise. It was important that the level of the material in the half pint paint can remained fairly constant for all blending. If the material amount was always 150 grams, the level within the paint can could vary based on the varying specific gravity of the material being blended. An advantage to mixing within the paint can was that it could be capped right away and serve as a storage container.

The only parameter to control was the temperature of the binder material being blended. The hot oil bath in which the paint can was immersed used high temperature oil specified to handle temperatures as high as 225°C, which was not out of the realm of possibility because of the RAS binder viscosity – temperature relationship.

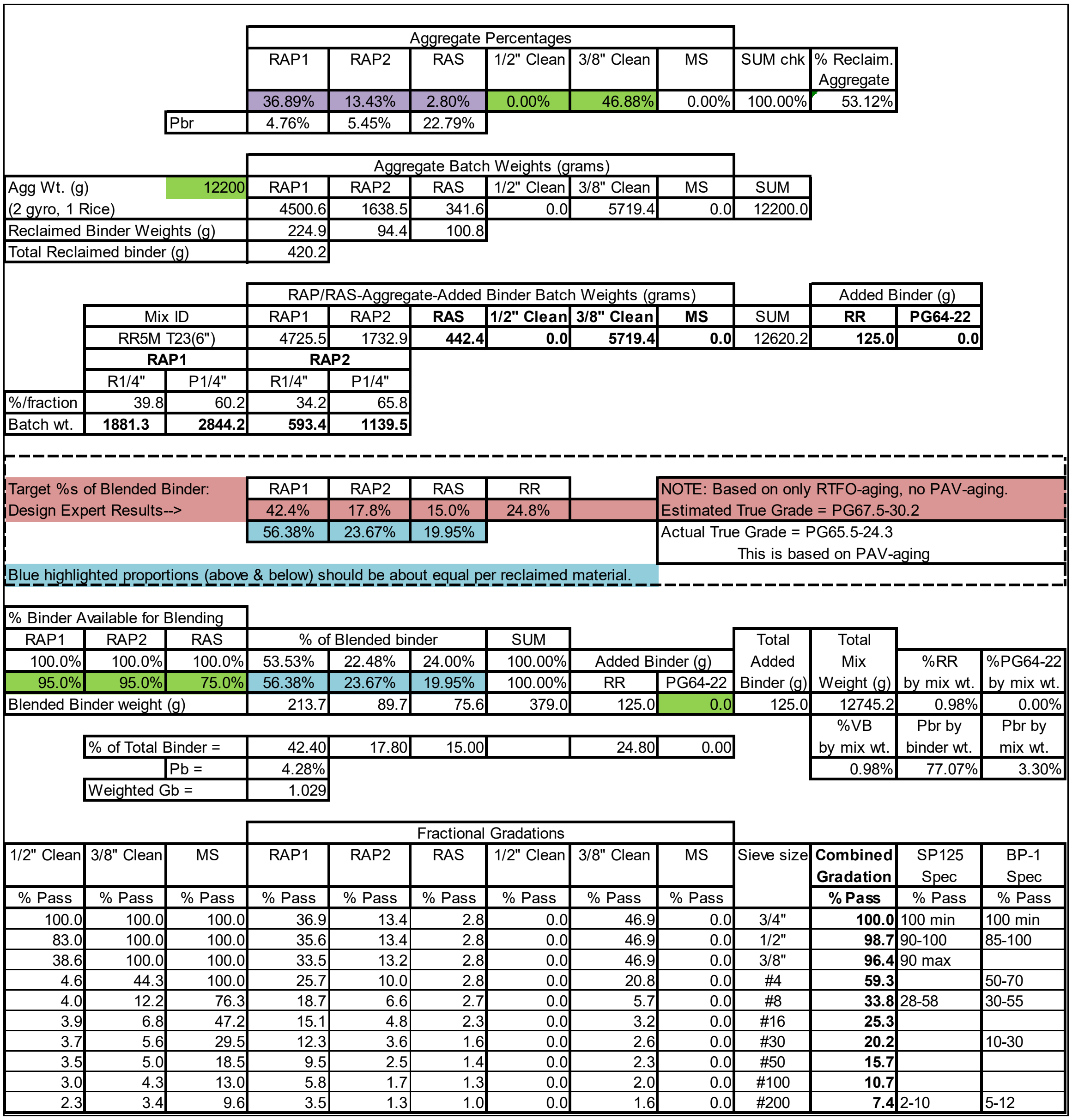
The choice of a mixing time was somewhat arbitrary although it seemed logical to start the time period once the temperature of the material in the paint can had stabilized to the point that the viscometer torque verified the viscosity of the material was steady at 170 (±20) centipoise. A mixing time of 15 minutes seemed adequate but not excessive, although plant produced HMA that contains RAP and/or RAS is mixed for a much shorter period of time. The mixing time using the Brookfield viscometer varied depending on the stability of the viscosity reading. For the higher temperature blends (e.g. RAP and RAS only blends), mixing time could last for 30 minutes or more.

APPENDIX E

FPM DESIGNS USING RR5 BINDER BLEND

FPM Designs Using RR5 Binder Blend

Using the verified RR5 blend, discussed in Section 3.1.5, a spreadsheet was developed to control the blended-binder grade and the aggregate gradation of the FPM. Figure E1 shows a major portion of the spreadsheet.



Aggregate Percentages

	RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	SUM chk	% Reclaim. Aggregate
	36.89%	13.43%	2.80%	0.00%	46.88%	0.00%	100.00%	53.12%
Pbr	4.76%	5.45%	22.79%					

Aggregate Batch Weights (grams)

		RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	SUM
Agg Wt. (g)	12200							
(2 gyro, 1 Rice)		4500.6	1638.5	341.6	0.0	5719.4	0.0	12200.0
Reclaimed Binder Weights (g)		224.9	94.4	100.8				
Total Reclaimed binder (g)		420.2						

RAP/RAS-Aggregate-Added Binder Batch Weights (grams)

Mix ID	RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	SUM	Added Binder (g) RR	Added Binder (g) PG64-22
RR5M T23(6")	4725.5	1732.9	**442.4**	**0.0**	**5719.4**	**0.0**	12620.2	**125.0**	**0.0**

	RAP1 R1/4"	**RAP1** P1/4"	**RAP2** R1/4"	**RAP2** P1/4"
%/fraction	39.8	60.2	34.2	65.8
Batch wt.	**1881.3**	**2844.2**	**593.4**	**1139.5**

Target %s of Blended Binder:	RAP1	RAP2	RAS	RR
Design Expert Results-->	42.4%	17.8%	15.0%	24.8%
	56.38%	23.67%	19.95%	

NOTE: Based on only RTFO-aging, no PAV-aging.
Estimated True Grade = PG67.5-30.2
Actual True Grade = PG65.5-24.3
This is based on PAV-aging

Blue highlighted proportions (above & below) should be about equal per reclaimed material.

% Binder Available for Blending

RAP1	RAP2	RAS	% of Blended binder			SUM	Added Binder (g) RR	Added Binder (g) PG64-22	Total Added Binder (g)	Total Mix Weight (g)	%RR by mix wt.	%PG64-22 by mix wt.
100.0%	100.0%	100.0%	53.53%	22.48%	24.00%	100.00%						
95.0%	95.0%	75.0%	56.38%	23.67%	19.95%	100.00%						
Blended Binder weight (g)			213.7	89.7	75.6	379.0	125.0	0.0	125.0	12745.2	0.98%	0.00%
										%VB by mix wt.	Pbr by binder wt.	Pbr by mix wt.
	% of Total Binder =		42.40	17.80	15.00		24.80	0.00		0.98%	77.07%	3.30%
		Pb =	4.28%									
	Weighted Gb =		1.029									

Fractional Gradations

1/2" Clean	3/8" Clean	MS	RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	Sieve size	**Combined Gradation**	SP125 Spec	BP-1 Spec
% Pass	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass		**% Pass**	% Pass	% Pass
100.0	100.0	100.0	36.9	13.4	2.8	0.0	46.9	0.0	3/4"	**100.0**	100 min	100 min
83.0	100.0	100.0	35.6	13.4	2.8	0.0	46.9	0.0	1/2"	**98.7**	90-100	85-100
38.6	100.0	100.0	33.5	13.2	2.8	0.0	46.9	0.0	3/8"	**96.4**	90 max	
4.6	44.3	100.0	25.7	10.0	2.8	0.0	20.8	0.0	#4	**59.3**		50-70
4.0	12.2	76.3	18.7	6.6	2.7	0.0	5.7	0.0	#8	**33.8**	28-58	30-55
3.9	6.8	47.2	15.1	4.8	2.3	0.0	3.2	0.0	#16	**25.3**		
3.7	5.6	29.5	12.3	3.6	1.6	0.0	2.6	0.0	#30	**20.2**		10-30
3.5	5.0	18.5	9.5	2.5	1.4	0.0	2.3	0.0	#50	**15.7**		
3.0	4.3	13.0	5.8	1.7	1.3	0.0	2.0	0.0	#100	**10.7**		
2.3	3.4	9.6	3.5	1.3	1.0	0.0	1.6	0.0	#200	**7.4**	2-10	5-12

Figure E1. Original FPM Design using No PG64-22 Virgin Binder

The goals of the FPM design process were to achieve a blend of reclaimed and virgin materials (aggregates and binder, which includes the RR) that will 1) achieve the desired binder grade (e.g. PG64-22), 2) meet gradation specifications, and 3) meet FPM volumetric criteria (% air voids, % voids in the mineral aggregate or VMA, and % voids filled with asphalt or VFA).

The first items to point out in Figure E1 are the pink highlighted cells marked as “DesignExpert Results.” These are input cells for any verified binder blend component proportions. In this case, it is the component proportions for the verified RR5 blend discussed in section 3.1.5, 42.4% RAP1, 17.8% RAP2, 15.0% RAS, and 24.8% RR (or CycL for FPM comparative analyses).

The next step in using the spreadsheet is to decide the “% Binder Available for Blending” percentages (green cells, center-left). It cannot be overstated how much of an issue this is in the FPM paving industry today. The question of how much of the binder in the RAP/RAS is actually blending with virgin binder and contributing to the performance of the FPM continues to be the topic of major investigation at this time. Based on the literature and engineering judgment, the actual percentage of binder available for blending is less than 100% (complete binder availability) and much more than 0% (the “black rock” scenario). Therefore, based on many conversations with industry practitioners and experts, the RAP and RAS binder availability percentages were set at 95% and 75%, respectively.

The next step is to adjust the purple highlighted cells at the very top so that the light-blue highlighted cells directly above one another in the reclaimed materials columns are approximately equal per reclaimed material. This step adjusts the proportions of the reclaimed materials to keep the blended-binder grade at the desired level. At the same time, it changes the combined aggregate gradation and the reclaimed binder content.

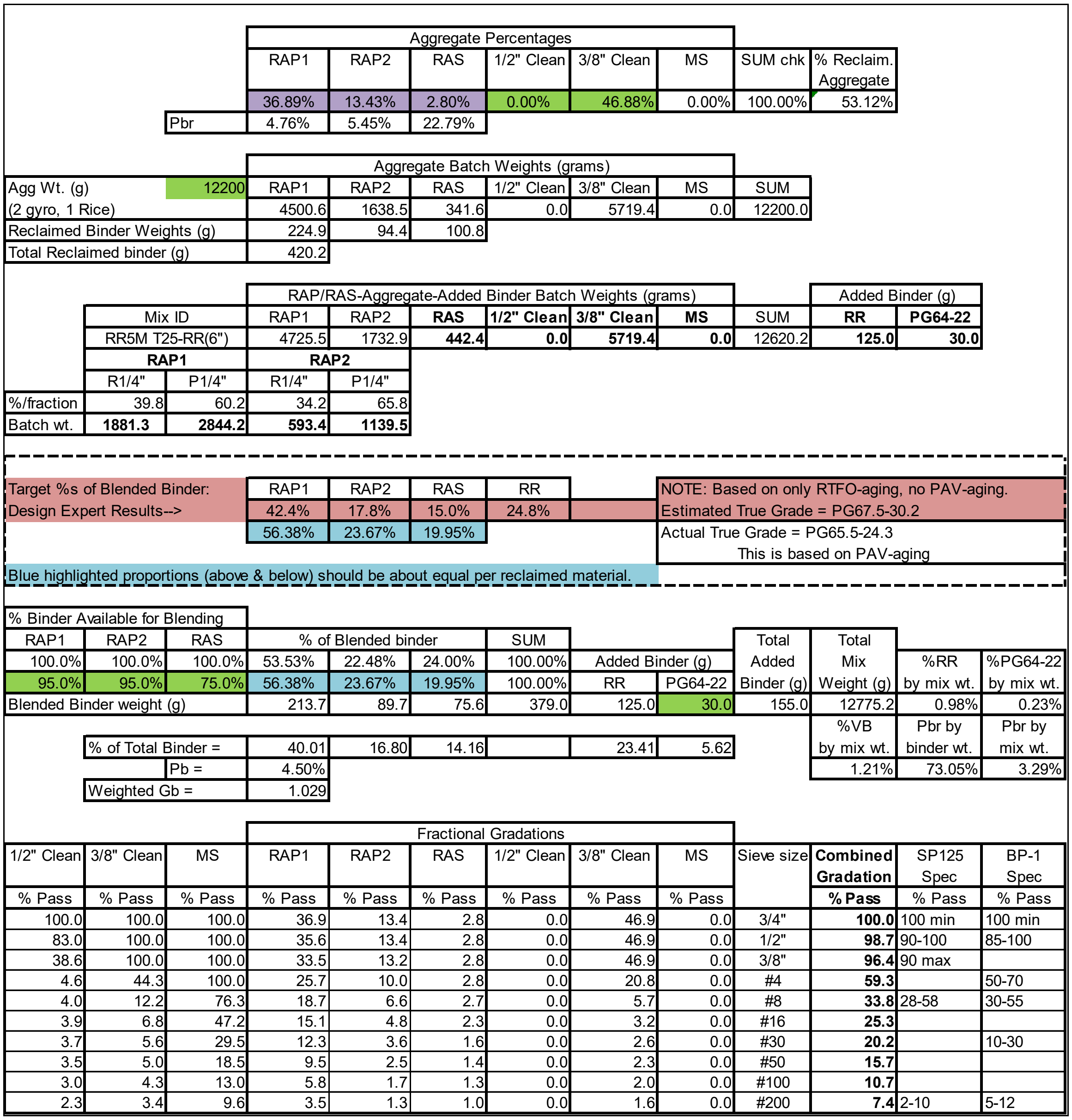
The next step is to adjust the virgin aggregate percentages to fine-tune the combined gradation. The aggregate percentages, reclaimed and virgin, must sum to 100%.

Finally, the total binder content as a percentage of the mix (P_b) can be adjusted upward by adding some virgin petroleum-based binder (e.g. PG64-22). On the other hand, if P_b is too high initially, the proportions of reclaimed materials can be lowered but in a manner that keeps the blended-binder grade at its desired level.

There is quite a bit of flexibility in this design process:

- There is choice in the binder blend proportions (DesignExpert solutions) that can produce a desired binder grade.
- The % Binder Available for Blending percentages can be changed if so desired.
- The number and gradation of the different virgin aggregates can be adjusted.
- The relative proportion of the reclaimed materials to the virgin aggregates can be adjusted.
- The reclaimed materials could be fractionated to provide much more control of the gradation.

Starting with the Figure E1 original (no-virgin-binder) design, an additional 30 grams of PG64-22 was added (i.e. P_b of 4.50%), and four batches of FPM were ultimately produced. Prior to batching the aggregates, the RAPs were split on the ¼ inch screen, producing fractionated RAPS or FRAPS. This was done in an effort to better control the gradation during batching. The design for this FPM with minimal PG64-22 virgin binder is shown in Figure E2.



	Aggregate Percentages							
	RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	SUM chk	% Reclaim. Aggregate
	36.89%	13.43%	2.80%	0.00%	46.88%	0.00%	100.00%	53.12%
Pbr	4.76%	5.45%	22.79%					

		Aggregate Batch Weights (grams)						
Agg Wt. (g)	12200	RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	SUM
(2 gyro, 1 Rice)		4500.6	1638.5	341.6	0.0	5719.4	0.0	12200.0
Reclaimed Binder Weights (g)		224.9	94.4	100.8				
Total Reclaimed binder (g)		420.2						

	RAP/RAS-Aggregate-Added Binder Batch Weights (grams)							Added Binder (g)	
Mix ID	RAP1	RAP2	**RAS**	**1/2" Clean**	**3/8" Clean**	**MS**	SUM	**RR**	**PG64-22**
RR5M T25-RR(6")	4725.5	1732.9	**442.4**	**0.0**	**5719.4**	**0.0**	12620.2	**125.0**	**30.0**

	RAP1		**RAP2**	
	R1/4"	P1/4"	R1/4"	P1/4"
%/fraction	39.8	60.2	34.2	65.8
Batch wt.	**1881.3**	**2844.2**	**593.4**	**1139.5**

	RAP1	RAP2	RAS	RR
Target %s of Blended Binder: Design Expert Results-->	42.4%	17.8%	15.0%	24.8%
	56.38%	23.67%	19.95%	

NOTE: Based on only RTFO-aging, no PAV-aging.
Estimated True Grade = PG67.5-30.2
Actual True Grade = PG65.5-24.3
This is based on PAV-aging

Blue highlighted proportions (above & below) should be about equal per reclaimed material.

% Binder Available for Blending									Total	Total		
RAP1	RAP2	RAS	% of Blended binder			SUM	Added Binder (g)		Added	Mix	%RR	%PG64-22
100.0%	100.0%	100.0%	53.53%	22.48%	24.00%	100.00%						
95.0%	95.0%	75.0%	56.38%	23.67%	19.95%	100.00%	RR	PG64-22	Binder (g)	Weight (g)	by mix wt.	by mix wt.
Blended Binder weight (g)			213.7	89.7	75.6	379.0	125.0	30.0	155.0	12775.2	0.98%	0.23%
										%VB by mix wt.	Pbr by binder wt.	Pbr by mix wt.
% of Total Binder =			40.01	16.80	14.16		23.41	5.62		1.21%	73.05%	3.29%
		Pb =	4.50%									
Weighted Gb =			1.029									

			Fractional Gradations									
1/2" Clean	3/8" Clean	MS	RAP1	RAP2	RAS	1/2" Clean	3/8" Clean	MS	Sieve size	**Combined Gradation**	SP125 Spec	BP-1 Spec
% Pass	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass	% Pass		**% Pass**	% Pass	% Pass
100.0	100.0	100.0	36.9	13.4	2.8	0.0	46.9	0.0	3/4"	**100.0**	100 min	100 min
83.0	100.0	100.0	35.6	13.4	2.8	0.0	46.9	0.0	1/2"	**98.7**	90-100	85-100
38.6	100.0	100.0	33.5	13.2	2.8	0.0	46.9	0.0	3/8"	**96.4**	90 max	
4.6	44.3	100.0	25.7	10.0	2.8	0.0	20.8	0.0	#4	**59.3**		50-70
4.0	12.2	76.3	18.7	6.6	2.7	0.0	5.7	0.0	#8	**33.8**	28-58	30-55
3.9	6.8	47.2	15.1	4.8	2.3	0.0	3.2	0.0	#16	**25.3**		
3.7	5.6	29.5	12.3	3.6	1.6	0.0	2.6	0.0	#30	**20.2**		10-30
3.5	5.0	18.5	9.5	2.5	1.4	0.0	2.3	0.0	#50	**15.7**		
3.0	4.3	13.0	5.8	1.7	1.3	0.0	2.0	0.0	#100	**10.7**		
2.3	3.4	9.6	3.5	1.3	1.0	0.0	1.6	0.0	#200	**7.4**	2-10	5-12

Figure E2. FPM Design with Minimal PG64-22 Virgin Binder

The percentages of the -¼ inch (percentage passing the ¼ inch screen or P1/4″) and +¼ inch (percentage retained on the ¼ inch screen or R1/4″) for each RAP were determined and, during batching of the RAPs, the P1/4″ and R1/4″ fractions were recombined at the same percentages. This was done to assure that the RAP binder properties were not changed; i.e. without knowing the binder content and grade of each FRAP, recombining them in proportions other than the original percentages could have affected the total reclaimed binder content and/or blended binder grade.

Discussions of the results of the FPM designs shown in Figures E1 and E2 are given in Section 3.1.6.1.

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VITA

Steven Michael Lusher was born in St. Louis, Missouri on March 13, 1954, to Loretta and Donald Lusher. Mike's high school graduation took place in 1972 in his hometown of Union, Missouri. After work as a self-employed musician and a lengthy career as an over-the-road truck/bus driver, Mike returned to school to obtain a secondary education. He received his associate degree in Pre-Engineering from East Central College in Union, Missouri in May, 1993. He then transferred to the University of Missouri-Rolla (now Missouri University of Science and Technology, or Missouri S&T). In December, 1996, he received his bachelor's degree in Civil Engineering from the Department of Civil, Architectural, and Environmental Engineering (CArEE). In August, 2004, Mike received his master's degree in Civil Engineering with a focus on construction materials, also from the CArEE Department. In May, 2018, Mike received his PhD in Civil Engineering (construction materials) from the CArEE Department at Missouri S&T.

Beginning in January, 1998, Mike was co-director of the technician training and certification program held at Missouri S&T, which operated under the authority of the Missouri Department of Transportation Technician Certification Program. He was a senior research specialist in the CArEE Department for 12 years prior to receiving his PhD. Mike authored/co-authored publications including nine technical reports, one peer-reviewed conference paper, and two refereed journal papers prior to receiving his PhD.

Mike has been a long-time member of the American Society of Civil Engineers and a member of the Association of Asphalt Paving Technologists.