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# ***Louisiana Transportation Research Center***

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Final Report 560

## **Chemical Characterization of Asphalts Related to Their Performance**

by

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16. Abstract In this project the researchers studied a correlation between molecular structure and corresponding compositional analysis of asphalt binders of conventional hot mix asphalt mixtures (HMA) as well as mixtures containing reclaimed asphalt pavement (RAP) and/or recycled asphalt shingles (RAS) with their cracking potential at intermediate temperature. The molecular size and structure of asphalt components of RAP and RAS undergo large changes during their exposure to environmental factors, which affects the physical properties imparted to their mixtures with conventional asphalt liquids. The composition of the mixtures prepared using a PG 70-22M binder was ascertained using thin layer chromatography/FID detection (Iatroscan), gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR). The distribution of species by molecular mass as determined by deconvoluting gel permeation chromatographs, emphasizing in particular, the amount of asphaltenes as they are related to the age hardening of asphalt materials. The extent of sample aging is apparent from the carbonyl oxygen content from FTIR measurements of the mixtures. Fracture resistance of laboratory produced mixtures was assessed using the Semi Circular Bend Test (SCB) test procedure; a minimal value of 0.5 kJ/m <sup>2</sup> was considered acceptable. Mixtures containing up to 5% RAS, 15% RAP and 15% RAP/5% RAS met the SCB standard. Molecular fractionation through GPC of mixtures containing RAS confirmed the presence of highly associated asphaltenes in greater concentrations than mixtures containing recycled asphalt pavement (RAP). High concentrations of high molecular weight associated asphaltenes (mol wt > 20K Daltons) which are present in RAS samples decrease the fracture resistance of the asphalt mixtures. The use of recycling agents, Cyclogen-L, Hydrogreen, Asphalt Flux and Re-refined engine oil bottoms (REOB), did not reduce the concentration of the highly associated asphaltenes, further they failed to improve the cracking resistance of the asphalt mixtures evaluated in this study. However, the recycling agents effected quantitative extraction of the RAS asphalt component.			
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## ABSTRACT

This research was performed to study the use of recycled asphalt pavements (RAP) and recycled asphalt shingles (RAS) along with virgin binder for new road pavements. This is an environmentally friendly way to recycle the used asphalt. However, there is no established method for the proper usage of recycled material to produce products with predictable performances. In this project the researchers studied a correlation between molecular structure of asphalt binders of conventional hot mix asphalt mixtures (HMA) containing recycled asphalts (RAS and /or RAP) and/or recycling agents and their cracking potential. The molecular size and structure of asphalt components undergo large changes during its exposure to environmental factors, which affects its physical properties. Gel permeation chromatography (GPC) was used to study the molecular size distribution and Fourier transform infrared spectroscopy (FTIR) was used to study the extent of oxidation (aging) changes in the asphalt mixtures.

The distribution of species by molecular mass was determined by the GPC technique emphasizing in particular, the amount of asphaltenes as they are related to the age hardening of asphalt materials. The GPC data was correlated with the carbonyl oxygen content from infrared spectroscopic measurements of binders. Cracking potential was evaluated using the Semi Circular Bend Test (SCB) test procedure. Comparing this information in addition to other mix and binder physical properties with their chemical composition and/or their reactivity towards their immediate environment (such as air oxygen) should help establish a relationship to their performance in paving the roads. At present, there are neither methods to verify percentages of recycled asphalt use, nor to accurately predict the recycled asphalt binder blends from a design perspective without costly extractions. This work is intended to verify specification limits for recycled asphalt and new asphalt mixture blends and provide a method to identify recycled asphalt quantities in mixtures confirming design submittals.

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## IMPLEMENTATION STATEMENT

Since 1994, DOTD has specified the use of polymer-modified asphalt cements (PMAC) to improve asphalt pavement performance. However, several critical questions associated with QC analysis of PMAC remain unsolved. The overall goals of the project as stated in the proposal were met. The findings of this research are documented in this report. Specific accomplishments include:

- Development of an effective asphalt binder extraction methodology without affecting the binder properties
- Illustration of the forensic application of GPC to resolving mix problems encountered in the field
- Application of the GPC currently used by DOTD for quality control of the liquid asphalt binders received for testing by the Materials Lab
- Conduction of forensic evaluations using the GPC on several DOTD construction projects
- Continued support by the LSU Chemistry department using the GPC to evaluate and compare additional properties of the liquid binder to improve performance through a continuing research study, LTRC 12-3B
- Detailed analysis of DOTD quality control GPC chromatograms of the liquid binders received for testing by the Materials Lab, where the polymer, asphaltenes and maltenes contents of each sample are compiled for use as a reference
- Extraction and characterization of RAP and RAP mixes with virgin binders
- Extraction and characterization of RAS and RAS mixes with virgin binders
- Extraction and characterization of RAP/RAS mixes with virgin binders
- Deconvolution of GPC chromatograms to refine the understanding of asphaltenes distribution in RAP and RAS mixes
- Evaluating the impact of recycling agents on properties of mixes containing RAP and RAP/RAS blends



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# INTRODUCTION

## Background and Significance of the Research

More than 90% of the roads in the U.S. are covered with asphalt mixtures and over 90% of U.S. highways and roads are constructed with hot mix asphalt (HMA). The asphalt industry produces about 500 million tons of HMA annually in the U.S. [1], [2]. It consumes a great amount of resources (aggregates and asphalt) and energy (production and transportation). Asphalt is a mixture of wide variety of chemical compounds that include aliphatic hydrocarbons and highly fused aromatic ring systems. To improve the final properties of an asphalt binder, a high molecular weight polymer such as polystyrene-*b*-polybutadiene-*b*-polystyrene, a block copolymer (SBS) and/or polystyrene-polybutadiene rubber (SBR) is added to produce polymer modified asphalt cements, PMACs. The polymer modified asphalt binder can be regarded as a true solution in which the polymer is homogeneously blended with the components of the base asphalt cement.

The crises that the U.S. and Louisiana face now present a challenge to the asphalt industry that will certainly require the development and implementation of new concepts and technologies in order to mitigate the series economic consequences associated with rehabilitation and or reconstruction of the affected highway infrastructure. Existing asphalt pavement materials are commonly removed during resurfacing, rehabilitation, or reconstruction operations. Once removed and processed, the pavement material becomes reclaimed asphalt pavement (RAP), which contains valuable asphalt binder and aggregate. RAP is most commonly used as an aggregate and virgin asphalt binder substitute in recycled asphalt paving, but it is also used as a granular base or sub base, stabilized base aggregate, and embankment or fill material. With increased demand and limited aggregate and binder supply, HMA producers have begun using RAP as a valuable component in HMA. Currently in Louisiana, 100% of RAP materials are being recycled into highway usage in one form or another. Although RAP can be used for various purposes such as granular shoulders, embankments or any form of filling materials, the preferred usage is as asphalt bound layer somewhere in the pavement structure.

There has been renewed interest in increasing the amount of RAP used in HMA. It is estimated that the average use of RAP across the U.S. is 12%. Less than half of State Transportation Departments use more than 20% RAP. According to State Transportation Department specifications, there is the potential to use up to 30% RAP in the intermediate and surface layers of pavements [2]. While majority of U.S. states permit the use of more

than 25% RAP in all or base and intermediate HMA layers, DOTD permits more than 25% RAP in base layers only. The performance and life of pavement containing up to 30% RAP is similar to virgin pavements with no RAP. However, with RAP contents greater than 25%, careful consideration should be given to the selection of the grade of asphalt binder added to the recycled asphalt mixture according to State Transportation Department specifications.

Despite similarities between producing virgin asphalt mixtures and RAP asphalt mixtures, there are still challenges for maximizing RAP use and routinely using high RAP. According to AASHTO M 323, the current binder selection guidelines for RAP mixtures were formulated based on the assumption that complete blending occurs between the virgin and RAP binders [3]. It is understood that the amount of blending that occurs between the virgin and RAP binder is somewhere between complete blending and no blending at all. There is, however, no direct method available to accurately determine the amount of blending that occurs. Currently, researchers are performing ongoing studies to develop methods to determine if proper blending has occurred by using mixture properties such as dynamic modulus to estimate blended binder properties and to compare estimate blended binder properties to measured binder properties. For high RAP mixtures, blending charts can be used to properly determine the virgin binder grade. They can also be used to optimize the amount of RAP used if the virgin binder grade is known. However, blending charts refer only to asphalt cements with no polymeric additives, viz., PMAC binders. Guidance on testing and designing with RAP in the Superior Performing Asphalt Pavements (Superpave<sup>®</sup>) mixture design method in the lab and field is available [4]. The work to determine RAP content require expensive, time-consuming laboratory binder extraction and recovery procedures, which is followed by testing of the recovered binder [5],[6]. Consequently, many State transportation departments are reluctant to permit RAP content that require this testing. As of 2007, about 40 million tons of RAP were reused or recycled into other pavement-related applications every year for a total use of over 100 million tons of RAP each year [1].

### **Recycled Asphalt Shingles**

Where appropriate, recycling of other construction materials in HMA makes sound economic, environmental, and engineering sense. This is the case of recycled asphalt shingles (RAS). EPA estimates that 11 million tons of waste shingles are generated every year in the U.S. The overwhelming majority of them are post-consumer, mostly from tear-offs. Asphalt shingle waste makes up 8% of the total building-related waste stream and up to 10% of construction and demolition debris. Tear-off shingle asphalt scrap is generated everywhere

throughout the nation during re-roof construction projects. The steady increase in cost and price of virgin asphalt is driving the interest in recycled supplements. Recycling the asphalt shingles is a growing industry that could divert millions of tons of materials from landfills while creating jobs and generating revenue. It has been estimated that recycling one ton of shingles is equivalent to avoiding the use of one barrel of oil [7]. The cost of disposal of asphalt shingles at recycling plants is generally less than at landfills, and asphalt shingles used in paving have been shown to reduce paving costs [8].

Asphalt shingles are the most popular roofing material and are utilized in roughly 67% of the U.S. residential roofing market. There are approximately 11 million tons of asphalt shingles disposed of each year in the U.S. RAS waste is comprised of ten million tons of installation scraps (tear-offs/post-consumer) from re-roofing, RAS-P, and one million tons of manufactured shingle waste (post-industrial waste), RAS-M [9]. RAS is comprised of asphalt binder (19–36%); fiberglass or cellulose backing (2–15%); sand-sized aggregate, ceramic-coated natural rock, (20–38%); and mineral filler or stabilizer that includes dolomite, limestone, and silica aggregates (8–40%) [7], [10], [11]. Recent estimates indicate that recycled asphalt shingles contain 15–35% of asphalt binder, which may provide an annual savings of \$1.1 billion and reduce nonrenewable energy consumption in the U.S. [9], [10]. The use of RAS in asphalt mixtures reduces the negative impacts on the environment associated with the extraction, transportation, and processing of virgin materials. It also preserves valuable landfill space while allowing state agencies/owners to offset some of the extra costs caused by the increase in aggregate and petroleum prices.

Since the early 1990s, a number of research studies evaluated the use of RAS in HMA and its influence on the mix mechanical behavior. The use of RAS in hot-mix asphalt is expected to provide significant benefits to the asphalt industry and highway agencies by reducing the amount of virgin asphalt binder that is added to the mixture. Air-blown asphalt is typically used in the manufacturing of asphalt shingles; this type of asphalt binder has a greater viscosity than regular asphalt binder used in HMA [12]. Button et al. evaluated the influence of adding 5–10% of asphalt shingles on the mechanical properties of asphalt mixtures as compared with untreated mixes [11]. The use of RAS resulted in a decreased tensile strength and creep stiffness of the mixture but it improved the mix resistance to moisture damage.

In spite of the potential benefits of the use of RAS in asphalt mixtures, many states are still cautious in the use of high RAS content in asphalt mixtures because of construction and durability concerns. To ensure the successful use of RAS, confidence in the mixture design procedure requires addressing many concerns related to the interaction between virgin and

recycled materials, which has an effect on the durability of the produced mixture.

### **Performance of RAS in Asphalt Pavements**

The industry has been addressing the stiffness and blending concerns by using softer binders when using higher RAP/RAS contents. Since fatigue cracking is influenced more by the intermediate temperature binder properties, using soft (modified) binders is an effective method to improve cracking resistance of RAS mixes. Zhou et al. conducted a comprehensive investigation of HMA mixes containing RAS [9]. This study characterized the RAS asphalt binder including the evaluation of blending charts for virgin/RAS binders. In addition, the impact of RAS content on the optimum asphalt binder content and respective engineering properties on mixtures containing RAS was evaluated. It was concluded that the use of RAS had no significant influence on dynamic modulus, but it improved mixture resistance to rutting and moisture damage. However, mixtures containing RAS had very poor cracking resistance as compared to mixtures containing no RAS. The authors explored two approaches to improve cracking resistance of mixtures containing RAS. It was stated that the use of soft binder and increasing the design density can improve cracking resistance. In terms of rutting and moisture damage, the use of soft binders was superior to increasing the design density. When using the softer binder and low air void approaches, one should be aware that, if the RAS is not well blended into the mixture or, if segregation occurs during mixing and/or placement, there will be spots on the pavement with "softer" mix, which may fail due to rutting [13].

With the increased interest in using RAS, the use of recycling agents is considered essential in order to soften and/or to rejuvenate the aged and stiff binders in RAS. Recycling agents are classified as two types: rejuvenating agents and softening agents. Asphalt rejuvenating and softening agents are manufactured to restore the rheological properties of the reclaimed asphalt binder by diffusing into it and restoring its colloidal structure and reconstituting its chemical components. Therefore, rejuvenators have been extensively used in pavement preservation to revive the hard and oxidized top layer by penetrating into the pavement and fluxing with the aged binder to balance the maltenes to asphaltenes ratio [14]. Softening agents lower the viscosity of the aged binder while rejuvenating agents are intended to restore the rheological and chemical properties of the aged binder [15]. Examples of softening agents include asphalt flux oil, lube stock, and slurry oil. Examples of rejuvenating agents include lubricating and extender oils, which contain a high proportion of maltenes constituents and low saturate contents that do not react with asphaltenes [15].

It is unquestionable that diffusion is the key factor in blending rejuvenators with asphalts.

Diffusion of rejuvenators in RAP binders has been of interest since the 1980s [16]. Although there is experimental evidence that the rejuvenators penetrated the RAP binders [16], [17], corresponding evidence on the impact of these agents on RAS is limited. Soohyok et al. studied the impacts of three different rejuvenators on mixtures containing various contents of RAS and RAP [17]. The authors used LWT, overlay test, repeated load test and dynamic modulus to characterize the mixtures. It was concluded that the rejuvenators improved the cracking resistance, moisture susceptibility, and rutting resistance comparatively to the control mixture. However, the ranking of the three rejuvenators used in the study depended on mixture types and properties evaluated.

### **Asphalt Characterization**

The composition of asphalt differs depending on the crude source and the refining process. The components of asphalt have been characterized as saturates, aromatics, resins, and asphaltenes (SARA) using extraction techniques to separate the components. The maltenes are low molecular weight (MW) mixtures (<3000 daltons), which act as dispersing agents for the higher molecular weight components. The maltenes are composed of saturates, aromatics, and resins, which can be separated by their differences in polarity. Asphaltenes are the bodying agent for the maltenes and have a significant influence on asphalt performance [18]. The largest "asphaltenes" are assemblies of smaller molecules held together by one or more intermolecular forces. Through changes in the polarity of the solvent used in the analysis, the ability of the samples to undergo self-assembly by different interactive mechanisms has been probed [19].

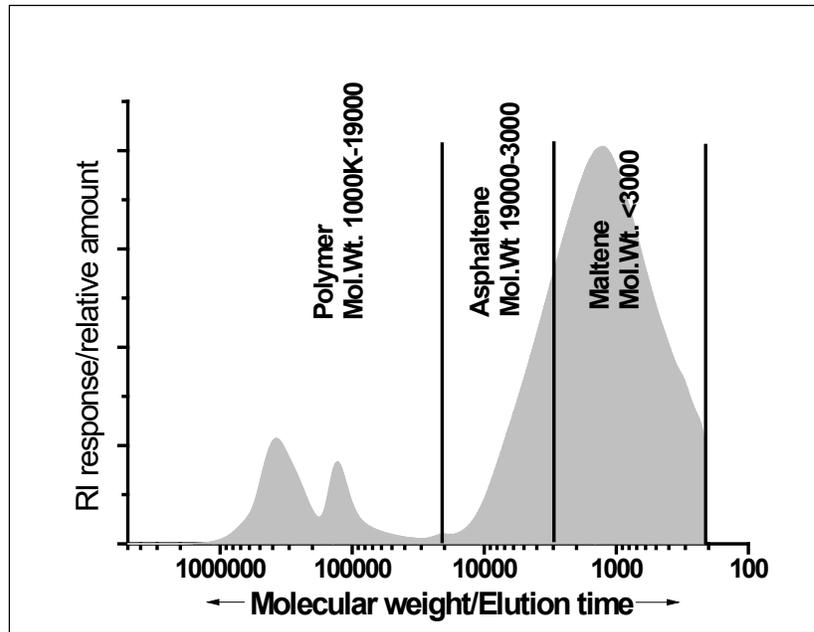
Analysis of the asphalt components is facilitated using an Iatroscan instrument, i.e. thin layer chromatography of the maltenes absorbed in silica rods and sequential elution with a series of solvents with increasing polarity. The concentration of the components in the elution bands is accessed by burning them from the rod and passing the gases through a Flame Ionization Detector (FID). The test method actually defines asphaltenes as the insoluble fraction recovered from n-heptane precipitation. The n-heptane soluble fractions (maltenes) can then be separated into three fractions and identified by the increasing polarity of the eluting solvents as saturates, aromatics, and resins [20], [21]. The asphaltenes fraction is precipitated with n-heptane and removed by filtration for gravimetric determination according to ASTM Method D-3279 "Standard Test Method for n-Heptane Insolubles." The heavy metals (typically vanadium and nickel) in the asphaltenes fraction tend to deactivate the silica coating on the chromatographic rods so it is preferable to remove the metals, before spotting the maltenes on the rods.

## **Gel Permeation Chromatography**

The differences in the molecular weights of maltenes and asphaltenes has prompted efforts to separate these components using Gel Permeation Chromatography (GPC). GPC provides a simple separation of molecules in a sample according to their sizes or, more specifically, their hydrodynamic volumes. This molecular size excluding technique can be likened to a sieving process in which largest materials elute first, followed by successively smaller molecules. The GPC ability to separate by molecular size rather than by some complex property such as solubility or absorptivity is one of the great advantages of the technique. This feature made GPC especially suited for fractionating complicated mixtures like crude oil residua, asphalts, and asphaltenes for nearly 50 years [22], [23], [24],[25]. GPC very uniquely mirrors the quantitative distribution of all species present in a binder, such as maltenes, asphaltenes, and polymers. The instrument signal, viz., the difference between the refractive indices of the eluting solution containing the asphalt and that of the solvent ( $\Delta RI$ ), is plotted versus the eluting volume (mL), (Figure 1). The molecules of larger size are excluded first, allowing the differentiation of asphalt species on the scale of  $MW = 10^6$ - $10^2$  Daltons. A correlation of the eluting volume with the molecular weight of the eluting fraction is achieved using narrow molecular weight standards [26].

Efforts to predict the properties of asphalts using GPC have been reported. Rather than estimate the actual molecular weight of the eluting fractions, the GPC chromatograms were divided into three regions: large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS). Researchers stated that the LMS and SMS regions were significant with respect to predicting pavement performance [27], [28], [29], [29], [30], [31], [32]. Although the arbitrary division of the chromatograms into arbitrary regions, the authors prefer to calibrate the GPC chromatograms and identify the maltenes, asphaltenes and polymer components on the basis of their molecular weight ranges [26]. Using molecular weight regions, it is possible to divide the MMS fraction into ranges which change when the asphalt ages or is modified.

As presented in Figure 2 for a PG 64-22 binder, quantification of asphalt components is readily made by determination of area of the respective eluted fraction calculated based on the fact that the area under the curve represents 100% of the sample molecules injected into the GPC system. The total GPC curve can be deconvoluted to show the contributions of the asphalt components using commercially available software, Origin 7 [33].

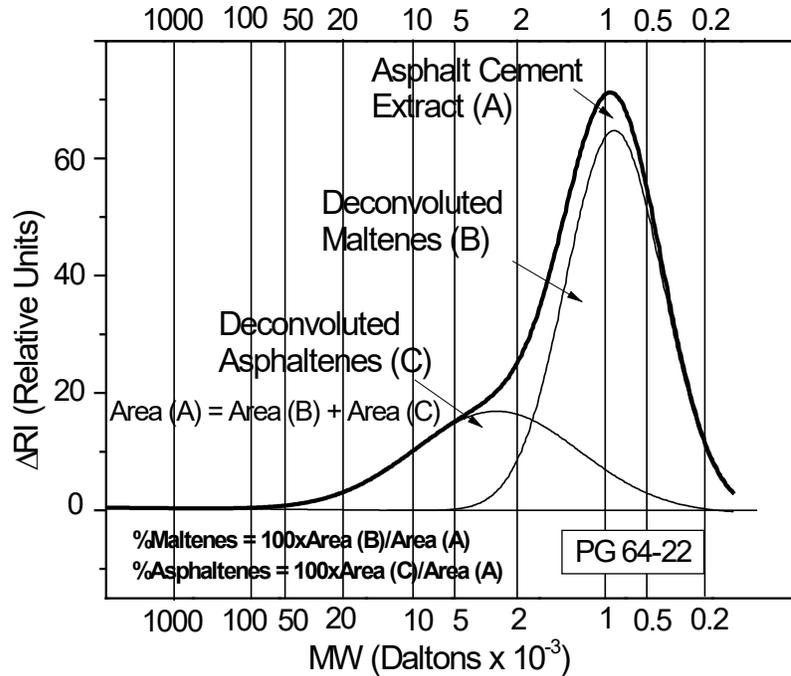


**Figure 1**  
**Molecular weight zones assigned in PMAC GPC chromatogram**

As indicated before, the first three eluted fractions are polymers (i.e., very high molecular weight, VHMW, with MW greater than 300,000 Daltons; high molecular weight, HMW, with MW between 45,000 and 300,000 Daltons; and medium molecular weight, MMW, with MW between 19,000 and 45,000 Daltons), followed by asphaltenes (molecular weight from 19,000 down to 3,000 Daltons), and maltenes (molecular weight less than 3000 Daltons) as presented in Figure 9. Quantitative data could be obtained by integration of the area under the curve as shown in Figure 10. For this project all integrations were performed using the Origin 7 or higher editions as follows.

The base line of the curve should be zero for the whole integration range. The integration Y column (B) is first normalized to 100% by creating a new Y column (column C), the values of which are obtained by dividing the integration column (column B) to the Y/100 number corresponding to that of the last X elution. For example, the 100% integral from Figure 2x was built by dividing the integration column Y (B) to 187/100. The percent maltenes are then calculated using normalized data by subtracting from 100 the integral value (read on normalized curve) corresponding to MW 3,000, viz., corresponding to X value (time) for MW 3,000 given by the calibration curve (shown in Figure 2). The percent asphaltenes were determined similarly by subtracting from the integral value corresponding to MW 3,000 the

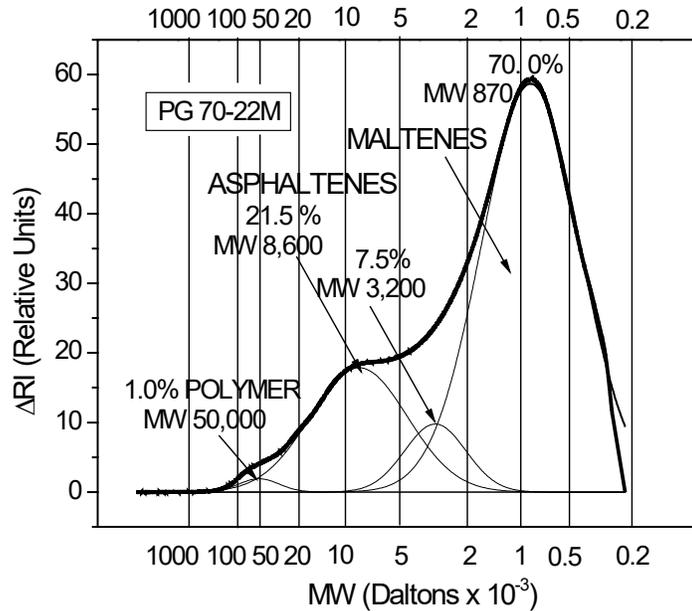
number for MW 19,000 given by the calibration curve of Figure 2, and so on for the higher MW fractions (polymers).



**Figure 2**

**Determination of maltenes and asphaltenes content of PG 64-22 binder by deconvolution of the GPC curve**

Earlier determinations by osmometry indicated that the average molecular weight MW of maltenes (as heptane soluble binder fraction) is 700-900 Daltons and that of asphaltenes (as heptane insoluble binder fraction) ranges between 2,000 and 10,000 Daltons [23]. These MW data have been confirmed by GPC method, which became a routine technique in Louisiana for analysis of asphalt binders [26]. Since the MW of polymers used in asphalt industry is higher than 10,000 Daltons, the polymer and asphalt components of polymer modified asphalt cements could be separated completely with accurate determination of molecular weight of species achieved by calibration with standard polystyrenes of narrow MW (Figure 3).



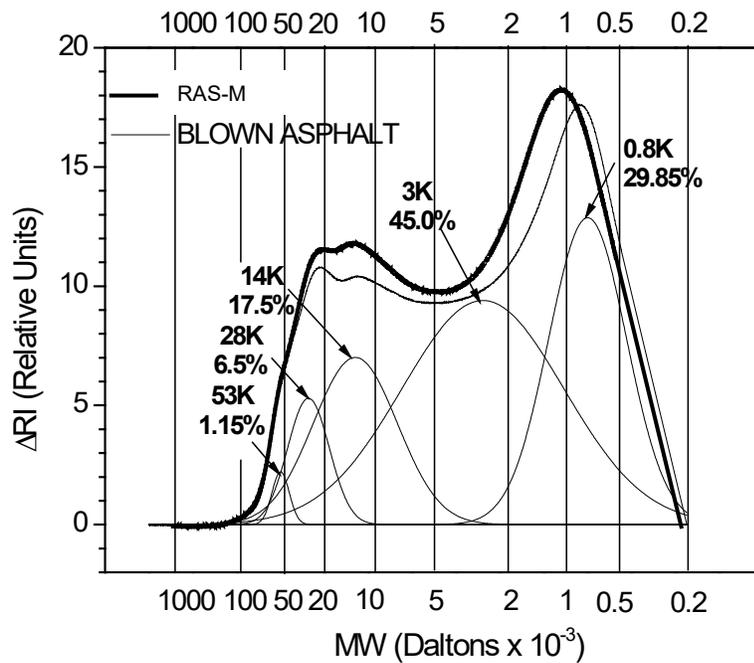
**Figure 3**

**GPC elution curve of PG 70-22M containing 1% polymer extracted from a mixture aged for 5 days at 85°C**

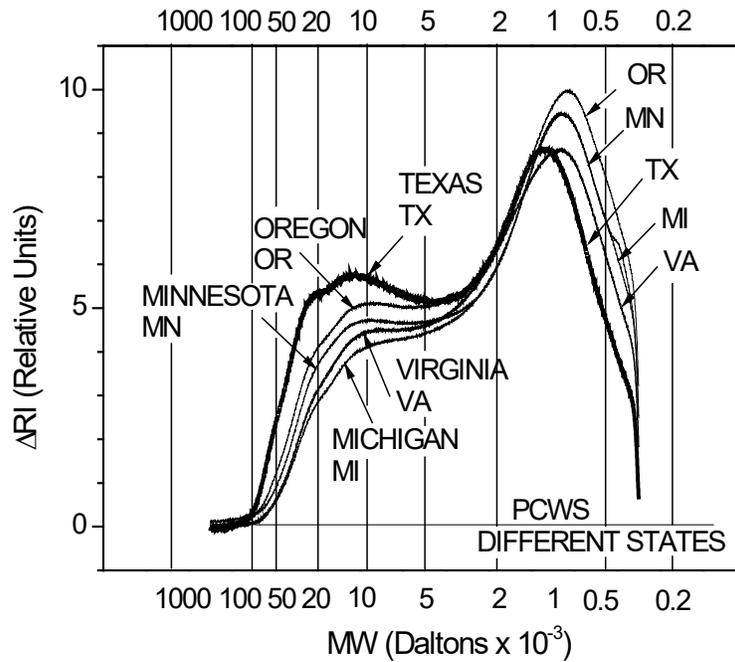
Asphalt aging is accompanied by significant changes in quantity and composition of the asphaltene fraction. The apparent molecular weight of the asphaltenes increases as the asphaltene molecules associate to form high molecular weight aggregated species. The presence of these species stiffens the asphalt binder leading to a corresponding hardening of the asphalt cement. Therefore, by analyzing the asphaltenes of asphalt paving combinations, such as asphalt cements and polymer-modified binders, with or without reclaimed asphalt materials (reclaimed asphalt pavement RAP, RAS), one might correlate physical performances of mixtures containing these materials with the content and magnitude of asphaltene species apparent molecular weights.

RAS material can be generated from either post-consumer (shingles that have been in service on roofs and have been removed), (RAS-P), or manufactured waste (produced during manufacture of new shingles), (RAS-M). The material used to manufacture roof shingles is highly oxidized blown asphalt as confirmed by the GPC chromatograms; the assemblies of asphaltene species from blown asphalt and RAS-M are practically identical (Figure 4). In addition to oxidation, the blowing process increases the asphalt aromaticity (conjugation) and average molecular size, which improves opportunities for self-assembly. A bi- or tri-modal peak shape showing the presence of two or three distinct populations of molecular sizes is regarded as evidence of intermolecular association in the large molecular size (LMS) region

on the left of the chromatogram [19]. Over 25% of associated asphaltenes in blown asphalt and RAS-M have an apparent average MW's of 10K-50K Daltons. Asphalt binders extracted from manufactured waste (RAS-M) and post-consumer waste shingles (RAS-P) typically have different properties because of the aging of the later that occurs on a roof. A further major concern with using recycled asphalt shingles relates to the variability in the properties of the RAS materials originating from different sources [34, 35]. GPC chromatograms from a survey of five sources of RAS-P collected from recycling plants around the country: Texas, Michigan, Minnesota, Oregon, and Virginia are shown in Figure 5.



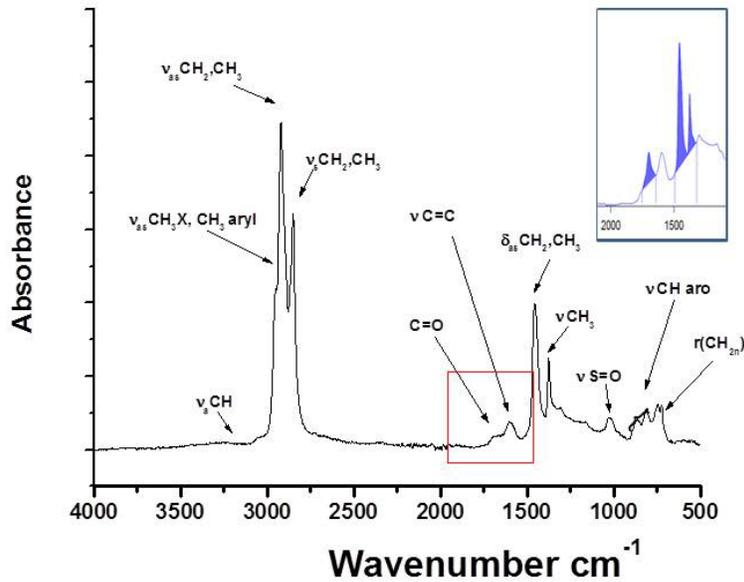
**Figure 4**  
**GPC data of Blown asphalt and RAS-M (RAS M) extracted binders**



**Figure 5**  
**GPC traces of RAS binders extracted from RAS-P of different sources**

### **Asphalt Characterization Using FTIR**

The characterization of oxidative asphalt aging with FTIR has been studied extensively in the past few years. The formation of carbonyl (C=O) containing molecules, which can be identified in the FTIR spectrum has been correlated with standard asphalt binder ageing techniques, RTFO and PAV [36]. It is well established that the main process occurring during this period is the oxidation of asphalt molecules which then leads aggregation due to the strongly interacting oxygen containing molecules [37],[ 38]. Since the main process is oxidation, the oxidized species can be used to quantify the amount of aging. FTIR spectra of the aged samples show a peak around 1700 cm<sup>-1</sup> which is the characteristic of C=O species. A typical spectrum of an aged asphalt sample is shown in Figure 6, showing the key absorption bands.



**Figure 6**  
**Typical FTIR spectrum of an aged asphalt**

In the researchers previous investigations related to aging of SBS copolymer modified asphalt cements, FTIR was used to gain a relative understanding of oxidation, which is directly related to asphalt binder aging [39]. It was observed that the area of the carbonyl absorbance occurring at  $1700\text{ cm}^{-1}$  increased as compared to that of the C-C absorbance occurring at  $1455\text{ cm}^{-1}$ . The ratio of the C=O and C-C vibrations gave a relative comparison of how much oxidation is occurring. It was called carbonyl index.

$$\text{Carbonyl index} = \frac{\text{Area of the carbonyl centered around } 1700\text{ cm}^{-1}}{\Sigma \text{ Area of the spectral bands between } 1490\text{ and } 1320\text{ cm}^{-1}}$$

The carbonyl (CO) index correlated with a higher level of oxidation in the asphalt binder and a stiffening of the binder was observed [39]. Since both RAS-M and RAS-P are highly oxidized materials, it is expected that the carbonyl indices of paving asphalts incorporating RAS-M and RAS-P to be large. A correlation of CO index and the size and distribution of asphaltenes given by the maltenes/high end asphaltenes ( $\text{MW} > 10\text{K Daltons}$ ) ratio might be attempted, to a limited extent, to predict the field performance at intermediate temperatures as reflected by the value of  $J_c$  integral. The carbonyl index for each sample discussed in this report is reported in Tables 6-9 (vide infra).

## **OBJECTIVE**

The objective of this work is to study the effect of adding recycled asphalt pavement (RAP), and recycled asphalt shingles (RAS), and/or, in some cases, recycling agents along with virgin asphalt in HMA mixtures. The molecular size and structure of asphalts undergoes large changes during its exposure to environmental factors, which affects its physical properties. Gel Permeation Chromatography (GPC) was used to study the molecular size distribution and Fourier Transform Infrared spectroscopy (FTIR) was used to study the extent of oxidation (aging) changes in the structure molecules in the asphalt mixtures. These data were correlated to the cracking potential of the mixtures to understand the effect of using RAP and/or RAS in HMA mixtures. Recycled samples (RAP and RAS) were tested using GC/MS to see if the samples have polycyclic aromatic hydrocarbons.



## SCOPE

A compilation of fifteen asphalt mixtures with 12.5 mm and nominal maximum aggregate size (NMAS) was evaluated in this study. Post-consumer waste shingles (RAS-P) and manufacturer waste shingles (RAS-M) were considered in this study. Four types of recycling agents (Hydrogreen, Cyclogen-L, asphalt flux, and re-refined engine oil bottoms (REOB)) were used. A soft binder, PG 52-28, was also included in the study. The mixture designations and constituents are defined below:

- 70CO – Conventional mixture containing PG 70-22 asphalt binder that's SBS modified, no RAP, no RAS, and no recycling agents;
- 70PG5M – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-M, no recycling agents;
- 70PG5P – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P, no recycling agents;
- 70PG5P5HG – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P, 5% Hydrogreen added by total weight of RAS-P;
- 70PG5P12CYCL – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P, 12% Cyclogen-L added by total weight of RAS-P;
- 70PG5P20FLUX – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P, 20% asphalt flux added by total weight of RAS-P;
- 52PG5P – Mixture containing PG 52-28 soft asphalt binder, 5% RAS-P, no recycling agents;
- 70PG15RAP – Mixture containing PG 70-22 asphalt binder that's SBS modified, 15% RAP, no recycling agents;
- 70PG5P15RAP – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P, 15% RAP, no recycling agents;
- 70PG5PHG15RAP – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P, 15% RAP, Hydrogreen recycling agent added at 5% by total weight of RAS-P plus an additional 0.75% added by total weight of RAP; and
- 52PG5P15RAP – Mixture containing PG 52-28 soft asphalt binder, 5% RAS-P, 15% RAP, no recycling agents.
- 70PG5P\_B – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P (New Source), no recycling agents;
- 70PG5P\_B5SK – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P (New Source), 5% REOB;

- 70PG5P\_B10SK – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P (New Source), 10% REOB; and
- 70PG5P\_B15SK – Mixture containing PG 70-22 asphalt binder that's SBS modified, 5% RAS-P (New Source), 15% REOB.

SARA and GPC techniques were compared as procedures to analyze the differences between asphaltenes found in virgin asphalt binders and various RAS samples and RAP samples.

Cracking potential of the corresponding asphalt cements was evaluated using the SCB test at intermediate temperature. The percent content of polymers, asphaltenes and maltenes in aged polymer modified binders, as well as, that of asphalts containing RAS-M, RAS-P and RAP was reported. The potential impact of four rejuvenating agents, naphthalene oil (Cyclogen-L) and an abietic acid derived oil called Hydrogreen, a Newell flux and REOB was surveyed using SARA, GPC, and SCB analyses.

# METHODOLOGY

## Materials

Asphalt binders used in this study are PG 70-22, which is commonly used in Louisiana, PG 64-22, PG 52-28 (soft asphalt cement), and PG76-22 were acquired from a supplier within the state. The reclaimed asphalts used were recycled asphalt shingle (RAS) and recycled asphalt pavement (RAP). RAP materials were obtained from a contractor within the state which had reclaimed the RAP material from an existing State route. Two different types of RAS were used: post-consumer waste shingle (RAS-P) and manufactured waste shingle (RAS-M). Different rejuvenators used are Hydrogreen (a vegetable oil derived from pine tree pyrolysates) and Cyclogen-L (naphthenic oil), and asphalt flux (PG32.3-46.6). The softening agents utilized were a PG52-28 soft asphalt cement and an asphalt flux (PG28-46). The identity and properties pertinent to this report are compiled in Table 1.

**Table 1**  
**GPC molecular weight distribution, and carbonyl index, of materials used in blends**

Sample	Description	Total Polymer % 1000K - 19K	Asphaltenes % 300K - 45K	Asphaltenes % 45K - 19K	Asphaltenes % 19K - 3K	Maltenes % <3K	Carbonyl Index C=O
RA-1	PG52-28	0.36			17.65	81.99	-0.0058
RA-2	Hydrogreen	0			0.88	99.12	0.4
RA-3	Cyclogen-L	0	0	0	0	100	0.0606
RA-4	Asphalt Flux	0	0.13	0.51	24.85	74.47	0.0348
RA-5	Reclaimate Base Oil	0	0	0	0	100	0.0497
RA-6	Medium Neutral	0	0	0	0	100	0
RA-7	Hydrolene	0	0	0	0	100	0
RA-8	Recycled Engine Oil Bottoms		3.58	4.02	20.62	71.78	0.1246
RAS-P	Post-Consumer Waste Shingles	15.56			32.04	52.4	0.22
RAS-M	Manufactured Waste Shingles	13.18			32.85	53.97	0.25
RAP	Recycled Asphalt Pavement	2.06			27.83	70.11	0.1691

Limestone, gravel, granite, and natural sand aggregates commonly used in Louisiana were utilized in this study. Solvents, carbon disulfide (CS<sub>2</sub>), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dichloromethane (DCM), and iso-octane were obtained from Fisher Scientific and butylated hydroxytoluene from Sigma Aldrich. For PAH calibration, a 16 component PAH standard mix in dichloromethane (2000 µg/mL per component) was obtained from Sigma Aldrich (QTM PAH mix). The standards in the mixture were naphthalene, acenaphthylene, acenaphthene, 2-bromonaphthalene fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene. Bromonaphthalene, present in the mixture, is not one of the PAHs that are found in asphalt. Benzo[*b*]fluoranthene was missing in the PAH mixture and hence its presence could not be analyzed.

This report also describes samples analyzed at DOTD which are acquired from different companies in Louisiana.

### **Mixture Design**

During the asphalt mixture design process, the optimum asphalt cement content is determined by varying the virgin binder content while utilizing the same composite aggregate blend until volumetric and densification criteria are met. With the optimum percent binder content of the mixture and the percentage of virgin binder utilized being known, the actual %RAP and/or %RAS binder contribution in the total binder can be calculated for each mixture. In addition, the actual recycle asphalt availability binder factor, the % RAP and/or %RAS in the binder, and the recycle binder ratio (RBR), can be determined. The RBR is defined as the actual %RAP and/or %RAS binder contribution divided by the design optimum asphalt cement content. For economic benefits it is important to increase the RBR. Recycling agents were employed to increase the RBR for mixtures containing RAP and/or RAS. Recycling agents were introduced at various rates to maximize the RBR. Generally, the dosage rate for the RAs were selected because at the selected dosage all available recycled asphalt binder was utilized and the asphalt mixtures met the volumetric and densification criteria. Table 2 is a recapitulation of the %RAP and/or %RAS binder availability and the RBR for the mixtures evaluated in this study.

Table 2 presents a summary of the various binder contents and ratios used in the research. It is shown in Table 2 that the RBR is 9.4%  $[(0.5/5.3)*100]$  for 70PG5P, which contains no recycling agents. For economic benefits, it is important to increase the RBR. However, an increase in RBR could adversely affect the durability performance of asphalt mixtures, intermediate and low-temperature, respectively. Recycling agents were employed to increase

the RBR for mixtures containing RAS and/or RAP. Table 2 indicates that the RBR generally increased with the use of recycling agents.

**Table 2**  
**%RAS AC binder availability**

Mixture ID	Optimum Design Binder Content, %	RAS and/or RAP Asphalt Binder Contribution, %		Virgin Binder, %	Virgin Binder in Design, %	Actual % RAS and/or RAP Asphalt Binder Availability Factor	Recycled Binder Ratio, %
		Available	Actual				
70CO	5.3	0.0	0.0	5.3	100.0	0.0	0.0
70PG5M	5.3	1.3	0.6	4.7	88.7	46.2	11.3
70PG5P	5.3	1.4	0.5	4.8	90.6	35.7	9.4
70PG5P5HG	5.3	1.4	1.4	3.9	73.6	100.0	26.4
70PG5P12CYCL	5.3	1.4	1.2	4.1	77.4	85.7	22.6
52PG5P	5.3	1.4	0.7	4.6	86.8	50.0	13.2
70PG5P20FLUX	5.3	1.4	1.4	3.9	73.6	100	26.4
70PG15RAP	5.3	0.8	0.8	4.5	84.9	100	15.1
70PG5P15RAP	5.3	2.2	1.2	4.1	77.4	54.5	22.6
70PG5PHG15RAP	5.3	2.2	2.2	3.1	58.5	100.0	41.5
52PG5P15RAP	5.3	2.2	1.8	3.5	66.0	81.8	34.0
70PG5P_B	5.3	1.0	0.3	5.0	94.3	30.0	5.7
70PG5P_B5SK	5.3	1.0	0.8	4.5	84.9	80.0	15.1

Mixture ID	Optimum Design Binder Content, %	RAS and/or RAP Asphalt Binder Contribution, %		Virgin Binder, %	Virgin Binder in Design, %	Actual % RAS and/or RAP Asphalt Binder Availability Factor	Recycled Binder Ratio, %
		Available	Actual				
70PG5P_B10SK	5.3	1.0	0.9	4.4	83.0	90.0	17.0
70PG5P_B15SK	5.3	1.0	1.0	4.3	81.1	100.0	18.9

### Extraction of Binder from Mixes

For SARA analysis of asphalt binders from RAS, RAP, mixtures containing RAS with and without engineered additives, mixtures containing RAS, RAP, with and without engineered additives were extracted in accordance AASHTO T 164 “Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot Mix Asphalt HMA” – Method A [40]. Afterwards the solution of solvent (trichloroethylene) and asphalt binder obtained from AASHTO T 164 – Method A is then distilled to a point where most of the solvent is removed and then carbon dioxide gas is introduced to remove all traces of trichloroethylene. This procedure was conducted in accordance with AASHTO R 59 – “Standard Practice for Recovery of Asphalt Binder from Solution by Abson Method” [41].

Asphalt samples for GPC analysis were processed according to methodology described by Daly et al. [26]. The neat asphalts were dissolved in tetrahydrofuran (THF) to a concentration of 0.25-1.00%. The asphalts from mixtures were extracted with THF in closed vials at room temperature (by shaking), left overnight for decantation and filtered using 0.45 micron Teflon filters. The concentration of asphalt solutions was 0.5%. All samples were prepared the previous day and filtered in the day of analysis using 0.45 micron Teflon filters.

### SARA Analysis of Asphalt Binder Composition

Each binder was deasphalted according to ASTM Method D-3279 “Standard Test Method for n-Heptane Insolubles” to yield asphaltenes (As) and maltenes which are dissolved in the n-heptane soluble portion.

The maltenes were further fractionated on an Iatroscan TH-10 Hydrocarbon Analyzer to yield the composition in saturates (S), aromatics (Ar), and resins (R). n-Pentane was used to

elute the saturates, and a 90/10 toluene/chloroform mixture was used to elute the aromatics. The resins were not eluted and remained at the origin.

### **HMA Mixture Blending**

Upon the completion of the design phase of this study, aggregate blending calculations were performed to determine the weight of each dry aggregate component for a specific batch weight. After determination of each aggregate batch weight, aggregates were weighed and placed in flat pan. After batching, the aggregates was placed in a force draft oven at 163°C until such time that they reached this temperature. Approximately 1 hour before blending of the aggregate with the asphalt cement (AC) binder, the AC was placed in a force draft oven at 163°C. To assure uniform mixing all mixing equipment will also be placed in the force draft oven at 163°C prior to blending of aggregate and AC components. After all components reach the temperature of 163°C, these materials are placed in a mixing bucket. A crater in the center of the blended aggregate was formed for placement of the AC binder component at the specified batch weight. The mixing operation will follow immediately after the AC binder component is added to the aggregate to ensure uniform blending of the materials. After mixing the final HMA mixture was distributed in a flat pan and then placed back in a force draft oven at 163°C for 1 hour for short term aging. Upon completion of this step, the samples were prepared using the Superpave gyratory compactor to the specified dimensions for each particular test procedure.

### **Mixture Aging**

Mixture aging was performed according to AASHTO R30-02 (2010) [42] by placing compacted specimens in a forced draft oven for five days at 85°C. After aging, the specimens were loaded at an applied rate of -10°C/hour. The test was stopped either at -50°C (coolant limitation) or at fracture, whichever occurred first.

### **Sample Characterization Using Physical and Rheological Testing**

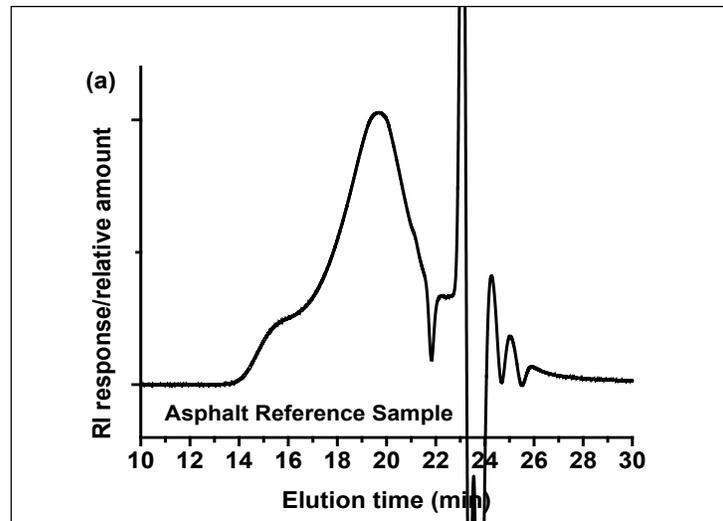
To evaluate performance, physical and rheological tests were determined on asphalt binders and hot mix asphalt mixtures (HMA) in a separate LTRC project [43]. In this LTRC project, in addition to asphalt cement rheology characterization, HMA mixture performance and characterization tests were conducted to define permanent deformation (stability), low temperature thermal cracking, and the fatigue life (durability) of HMA mixtures. The presence of RAS impacts the intermediate temperature binder properties that can be characterized using a Semi-Circular Bend (SCB) test to determine the critical strain energy ( $J_c$ ) [44, 45].

## Gel Permeation Chromatography (GPC)

GPC was performed using an EcoSEC high performance GPC system (HLC-8320GPC) of the Tosoh Corporation, equipped with a differential refractive index detector (RI) and UV detector. A set of four microstyragel columns of pore sizes 200 Å, 75 Å (2 columns) and 30 Å from Tosoh Bioscience was used for the analysis. Tetrahydrofuran (THF) at a flow rate of 0.35 mL/min. was used as the solvent. The solvent THF has a tendency to form highly explosive peroxides on storage in air. To minimize this problem, the solvent used for GPC analysis is stabilized with BHT. One gram of BHT is normally added to a 4L bottle of THF. Columns were calibrated using polystyrene standard mixtures PStQuick B (MW= 5480000, 706000, 96400, 10200, 1000), PStQuick E (MW= 355000, 37900, 5970, 1000), and PstQuick F (MW= 190000, 18100, 2500, 500) from Tosoh Bioscience. Details of the calibration procedure are described in the LTRC Report 505.

### GPC Sample Preparation and Analysis

Asphalt samples were dissolved in THF concentration of either 1% or 0.25%. All samples were prepared the previous day and filtered the day of analysis using 0.45 micron Teflon filters. The asphalt in the mix samples were extracted using THF solvent and filtered solution using 0.45 micron Teflon filters. The concentration of asphalt solution was 0.5%. Analysis of the samples using GPC: Tetrahydrofuran (THF) at a flow rate of 0.35 mL/ min. was used as the solvent; analysis time was 30 minutes. After the analysis, the chromatograms are base line corrected and peak edited using the GPC software and the molecular weights were generated using the calibration curve obtained using the polystyrene standards.



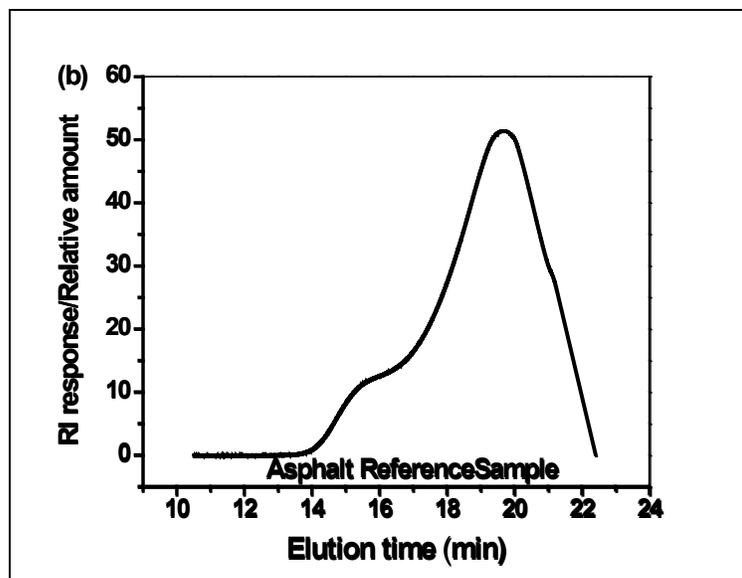
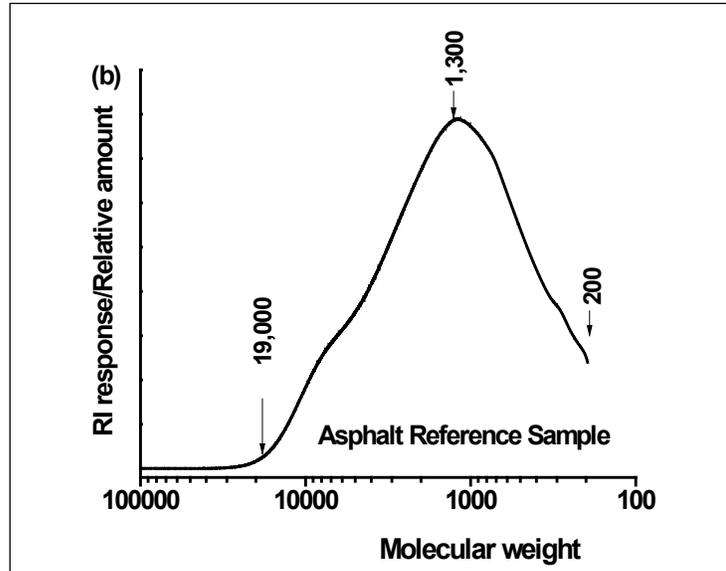


Figure 7

**Typical chromatogram of the asphalt reference sample (Company A): (a) complete curve and (b) reconstructed curve used for analysis**

A typical chromatogram of the 1% solution of the reference asphalt (Company A) in the THF solvent is shown in Figure 7. This is an example of asphalt that has no polymer added to it. Figure 7 presents the plot of the difference in refractive index between the solvent and the eluting solution (RI) versus the elution time as the data is collected. Note that the data above an elution time of 22 minutes includes RI responses relating to the air species, as well as to that of stabilizers present in the solvent. In analyzing this data, the RI response should be smoothed by extending the curve to the base line as shown in Figure 7b.

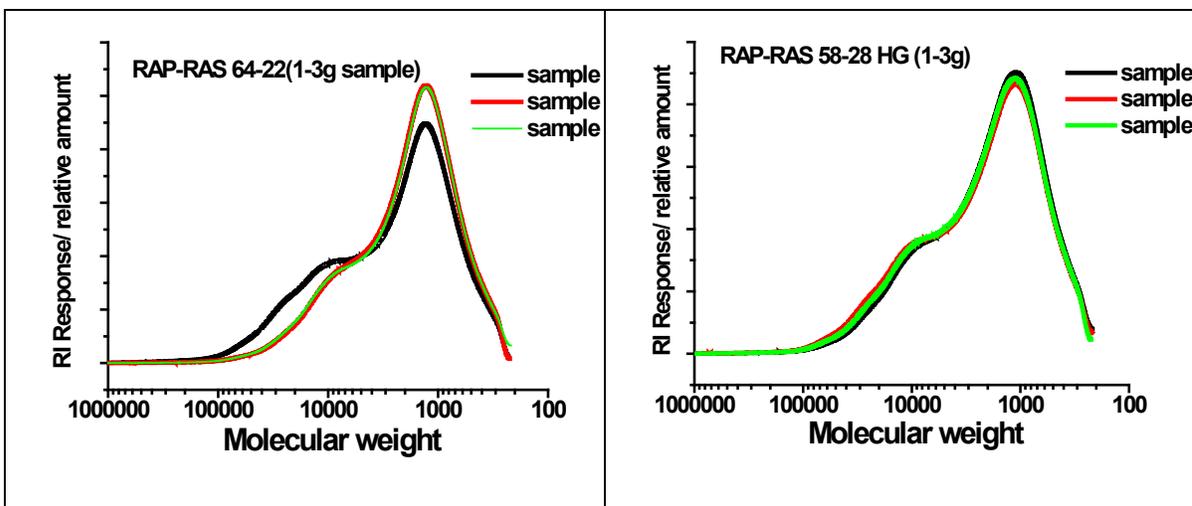
The retention times are then converted to molecular weights using the calibration curve obtained with polystyrene standards. Figure 8 shows that the typical asphalt components have molecular weights ranging from 19,000 to 200 Daltons (based on polystyrene molecular weights).



**Figure 8**  
**Retention times in the chromatogram shown in Figure 7 converted to a molecular weight distribution curve**

### Standard Deviation of Samples Analyzed by GPC

In the HMA process, the recycled asphalts (RAP, RAS, or both) are mixed with the virgin binder and aggregates, and sometimes with rejuvenating agents, to obtain a recycled asphalt mixture. It is expected that the hot-mix process generates a uniform mixing of these components. Triplicate samples gyratory compact samples of different mix asphalt were analyzed using GPC to see the uniformness of the components throughout the mixture. Standard deviation of three specimens of gyratory compact samples used to study three different notch depths were analysed using GPC. The three notch depths selected by LTRC researchers were 25.4 mm, 31.8 mm, and 38.0 mm. The standard deviation ranged from 0.1 to 6. The following GPC chromatograms (Figure 9) demonstrate typical examples of the comparison of the triplicate samples (curve of PG 64-22 containing RAP and RAS (5.6% PG 64-22 - RAP AC = 0.9, RAS AC = 0.6, LL) and RAP-RAS 58-28 HG-LL (5.4% PG 58-28HG -- RAP AC = 0.9, RAS AC = 0.6, LL)



**Figure 9**

**GPC chromatograms of a PG 64-22 containing RAP and RAS. (5.6% PG 64-22 -- RAP AC = 0.9, RAS AC = 0.6, LL) (SD =3.2, 1.8 &5.02) and RAP-RAS 58-28 HG-LL) (5.4% PG 58-28HG --RAP AC = 0.9, RAS AC = 0.6, LL) (SD = 0.9, 0.6, 1.5) supplied in triplicate**

The chromatogram or molecular weight distribution curve of each sample was divided into three regions of molecular weight to understand the distribution different molecular size species in each sample, i.e., molecules having size greater than 19,000, molecules having size between 19,000 and 3000, and molecules with size less than 3000 Daltons. Arbitrarily the first region can be considered as high molecular weight polymer and highly associated asphaltenes, the second region as asphaltenes and the third region as maltenes. In order to understand the variability of spread of data, the mean, standard deviation, and coefficient of variation of two different samples are calculated and the values reported in Table 3. The GPC chromatograms show that there can be certain amount of non-uniformity in some samples which may be due to the RAP/RAS component in the mixture, which does not melt completely and uniformly throughout the mixture. To compensate with this non-uniformity, all GPC results reported in this report are the average values of three runs.

**Table 3**  
**Triplicate Analysis of Samples of RAP/RAS Virgin Asphalt Mixes**

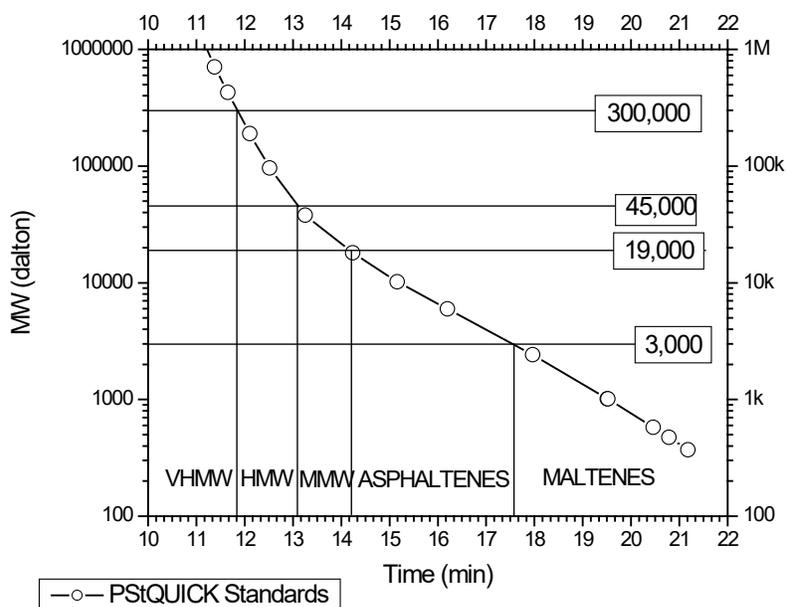
<b>GPC ID</b>		<b>Total Polymer + Associated Asphaltenes M.W &gt;19,000 %</b>	<b>Asphaltenes M.W 19,000-3000 %</b>	<b>Maltenes MW&lt;3000 %</b>
RAP-RAS 64-22-LL	SAMPLE-1	9.89	31.38	58.73
	SAMPLE- 2	4.17	28.25	67.58
	SAMPLE-3	4.50	28.23	67.27
	Mean	6.19	29.29	64.53
	SD	3.21	1.81	5.02
RAP-RAS 58-28 HG-LL	SAMPLE-1	5.57	28.96	65.47
	SAMPLE- 2	7.45	30.07	62.58
	SAMPLE-3	6.56	29.8	63.64
	Mean	6.52	29.61	63.89
	SD	0.94	0.58	1.46

### **Quantification by Integration of GPC Curves**

In most of the GPC studies on asphalt reported, the chromatogram curve is divided into three equal slices (or more) as large molecular size (LMS), medium molecular size (MMS) and small molecular size (SMS) [25], [29], [30]. It is also reported that the LMS region can be correlated with physical properties and field performance of the asphalt analyzed [31], [32], [46]. Many of these reports have not presented the range of molecular weight of these fractions in terms of polystyrene or other standards. Since the shape of chromatogram curve depends on the concentration of the injected sample, the solvent nature, column type, and other factors, it is difficult to make an accurate estimation of these values. T.J Morgan et al.

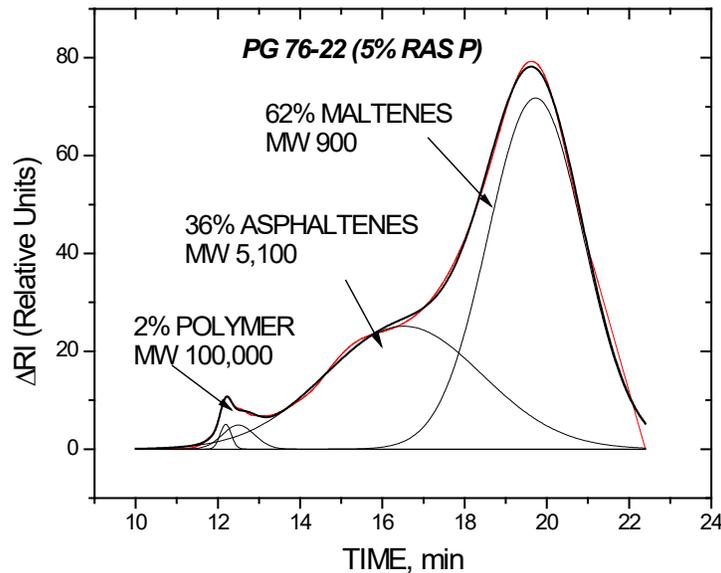
used laser desorption mass spectrometry (LD-MS) along with size exclusion chromatography (SEC) and planar chromatography to study the molecular weight of maltenes and asphaltenes of Maya crude oil [47]. The fractions were separated using extraction with pentane. The results revealed a small portion of asphaltenes extending to 10,000, and maltenes extending to 2000 molecular weights.

In this study, taking account of LMS, MMS, and SMS fractions and LD-MS values, the chromatogram was divided into five slices based on the molecular weight of the eluting species, and the calibration curve made using polystyrene standards Figure 10. [5], [39], [48]. The first three eluted fractions are polymers (i.e., very high molecular weight, VHMW, with MW greater than 300,000 Daltons; high molecular weight, HMW, with MW between 45,000 and 300,000 Daltons; and medium molecular weight, MMW, with MW between 19,000 and 45,000 Daltons), followed by asphaltenes (molecular weight from 19,000 down to 3,000 Daltons), and maltenes (molecular weight less than 3000 Daltons) as shown in Figure 10. Quantitative data can be obtained by integration of the area under the curve as shown in Figure 11. For this project, all integrations were performed using the Origin 7 software as described in Appendix A.



**Figure 10**  
**Molecular weight range of GPC asphalt fractions divided into five slices**



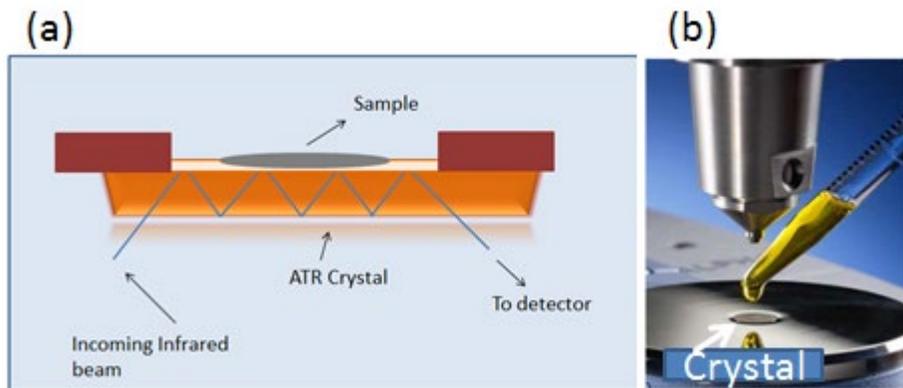


**Figure 12**  
**Deconvolution of the GPC curve corresponding to PG 76-22 (5% RAS-P) binder showing molecular weight and % composition determined by peak deconvolution technique**

### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is one of the more important methods for fingerprinting construction materials [49]. The researchers used an FTIR spectrometer in the Attenuated Total Reflectance (ATR) mode. In an ATR mode, the infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle (Figure 13) [50]. The internal reflection creates an evanescent wave that extends beyond the surface of the crystal, into the sample held in contact with the crystal. This evanescent wave extends only few microns ( $0.5\mu\text{-}5\mu$ ) beyond the crystal surface and into the sample. If the sample is placed in good contact with the surface of the crystal, the sample absorbs energy and the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in IR spectrometer. The detector then generates the IR spectrum. A graphical

representation of ATR phenomena (a) and an image of the real crystal (b) are shown in Figure 13.



**Figure 13**

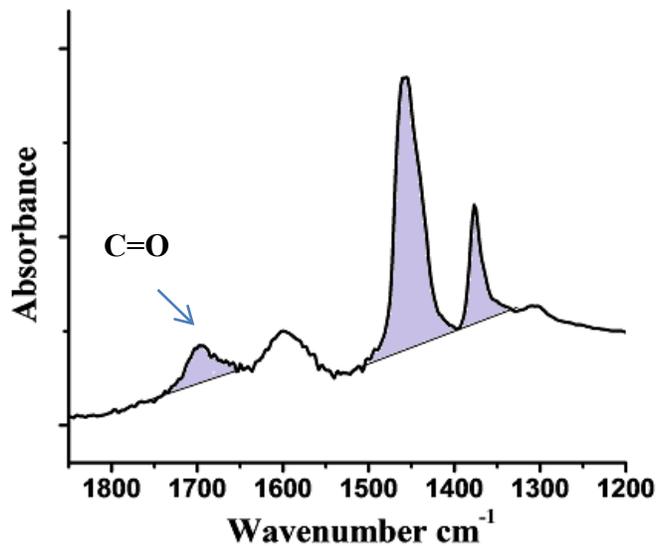
**(a) Graphical representation of ATR phenomena (b) an image of the real crystal (Bruker Optics alpha)**

FTIR spectra were obtained using a diamond single reflection attenuated total reflectance (ATR). An OPUS 7.2 data collection program was used for the data analysis. The following settings were used for data collection: 32 scans/sample, spectral resolution 4  $\text{cm}^{-1}$ , wave number range 4000-500  $\text{cm}^{-1}$ .

### **FTIR Sample Preparation**

The required amount of field cores samples was soaked in carbon disulfide for overnight. The solution was then filtered using a 0.45  $\mu$  filter. Normally 1% solution was prepared. A few drops of the solution were placed on the ATR crystal plate and the solvent allowed to evaporate. The spectrum was collected after the complete evaporation of the solvent. The carbon disulfide had peaks around 1500  $\text{cm}^{-1}$  and 2150  $\text{cm}^{-1}$ , which did not interfere with the characteristic peaks of asphalt. However, in all experiments the sample solution was allowed to dry for few minutes for the complete evaporation of the solvent. Samples containing RAP binder showed characteristic large peak around 1000  $\text{cm}^{-1}$  due to the Si-O bonds from the samples. This covers the S=O peak. This problem was solved by filtering the solution using 0.45  $\mu$  filter.

The RAP and RAS samples contained aged asphalt. It is well established that the main process occurring during this aging period is the oxidation of asphalt molecules which then leads aggregation due to the strongly interacting oxygen containing molecules. Since the main process is oxidation, the oxidized species can be used to quantify the amount of aging. FTIR spectra of the aged samples show a peak around  $1700\text{ cm}^{-1}$  which is the characteristic of C=O species (Figure 14). The carbonyl index was calculated from the band areas measured from valley to valley using the Bruker FTIR instrument OPUS spectroscopy software.



**Figure 14**  
**FTIR wave number spectrum range used for carbonyl index calculation**

However, some of the additive compounds with carbonyl group in their structure can distort the carbonyl index. Virgin asphalt PG 64-22 has no peak at the area near carbonyl absorption  $1700\text{ cm}^{-1}$ . However, the plant-derived rejuvenator, Hydrogreen, exhibits a substantial carbonyl peak at that area which can be attributed to the presence of esters and acid C=O functions in the rejuvenator. The FTIR measurement cannot separate these inherent ester C=O's from the carbonyls introduced by the aging process so the apparent carbonyl index of the mixtures containing Hydrogreen is a sum of the carbonyls from both the rejuvenator and the aged asphalt binder.

## **DISCUSSION OF RESULTS**

### **Asphalt Fingerprinting**

Asphalt from a given source of crude oil has its own characteristic chromatogram that slightly changes with grade. The addition of polymers to produce PG-70-22m or PG-76-22m does not change the fingerprint of the base asphalt. In fact, the unique characteristics of the polymer peak can be used to identify the type of polymer employed to produce the PMAC. The differences in shape and molecular weight distributions characteristic to radial polymers and linear ones can be a useful tool in qualitative identification of the polymer type used in addition to a quantitative GPC evaluation. Thus, GPC is a very effective method for detecting changes in the asphalt as a result of processing changes, crude oil changes, or changes in polymer content. In compiling a collection of asphalt samples from differing sources, it is essential that all GPC parameters remain constant. Columns may change their efficiency with time, and thus it is necessary to run the polystyrene standards periodically to confirm that the calibration curve has not changed.

A collection of data regarding the GPC characterization of paving asphalts and related materials (polymers and additives) from differing sources is presented in the Appendix B. Appendix B contains tables based upon GPC traces of samples analyzed by the Louisiana DOTD laboratory. Given that the GPC conditions are equal, characteristic chromatograms for Louisiana asphalt sources can be obtained. One should expect that the content of polymeric species in PMAC samples when analyzed by GPC to be 1-2% for PG 70-22m binders and 3-4% for PG 76-22m binders. Indeed, the average data collected at the DOTD Materials Laboratory tabulated in Appendix B, meets these expectations. The average asphaltenes content of PG-70 binders varied from ~12 – 17% even within binders from an individual supplier. This variation reflects variations in the crude source used to produce the asphalt. In general, the maltenes content ranged from 82-85%. The corresponding ranges from PG-76 asphalts were 15-16% for asphaltenes and 81-82% for maltenes.

### **Binder Characterization**

The SARA analysis of the binders described in this study is compiled in Table 4. The asphaltenes are reported as n-heptane insolubles and the maltenes comprised of resins, aromatics, and saturates were determined by TLC/FID with an Iatroscan instrument. Note that the asphaltene component as determined by precipitation under the SARA analysis heading, is considerably smaller than the sum of all the components with molecular weight

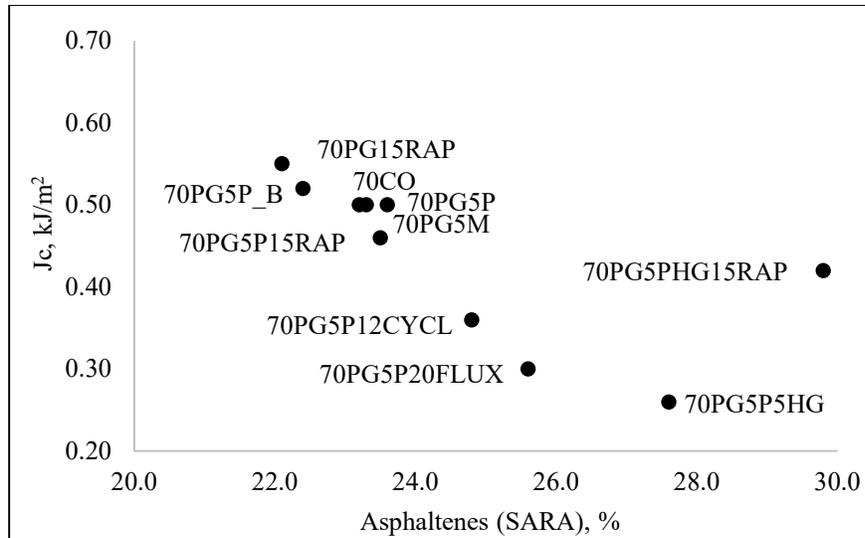
greater than 3,000 daltons estimated from deconvoluted GPC chromatograms and designated as DEC asphaltenes in Table 4. The higher percentage of DEC asphaltenes is composed of associated asphaltenes species with molecular weights as high as 100,000 [43]. The high molecular weight component (HMW) of the DEC asphaltenes, i.e. a sum of the species with molecular weights >20,000 Daltons, is also reported in Table 4. It is noted that the SARA asphaltenes analysis by precipitation does not capture the total amount of associated asphaltenes in the binder. Some associated asphaltenes remain in the resin fraction.

The correlation between the Iatroscan asphaltenes extracted from mixes prepared with PG70-22M and the cracking resistance of the mixes expressed by critical strain energy rate ( $J_c$ ) is shown in Figure 15. The precipitated asphaltenes appear to more accurately reflect the incompatibility of the higher molecular weight species that leads to lower cracking resistance. Although not shown, mixes containing REOB deviated substantially from the predicted relationship; both the apparent asphaltenes content of these mixes and the corresponding  $J_c$  was much lower. None of the mixes prepared using PG52-28 exhibited an acceptable cracking resistance. As shown in Figure 15, the percent asphaltenes increased in mixture 70PG5PHG15RAP as compared to mixture 70PG5P5HG. However, the  $J_c$  increased in mixture 70PG5PHG15RAP. The RAP binder is comprised of approximately 2% polymer which was beneficial in increasing the intermediate temperature performance of mixture 70PG5PHG15RAP as compared to mixture 70PG5P5HG.

**Table 4**  
**Chemical composition of extracted mixture binders**

Mix Designation	SARA Analysis, %					DEC ASPH, %	HMW, %	DEC MALT, %	J <sub>c</sub> , kJ/m <sup>2</sup>
	Asphaltenes	Resins	Aromatics	Saturates	Sum resins, aromatics, saturates				
70CO	23.2	32.7	42.4	1.7	76.8	30.0	1.0	70.0	0.5
70PG5M	23.3	36.0	39.4	1.7	80.1	34.0	3.0	66.0	0.5
70PG5P	23.6	26.7	46.0	3.7	76.4	39.0	5.7	61.0	0.5
70PG5P5 HG	27.6	30.0	39.3	3.0	72.3	41.0	8.5	59.0	0.3
70PG5P1 2CYCL	24.8	26.7	42.1	6.4	75.2	38.6	6.0	61.4	0.4
52PG5P	20.2	29.2	45.6	5.0	79.8	30.0	4.7	70.0	0.2
70PG5P2 0FLUX	25.6	22.8	44.2	7.5	74.5	35.3	6.0	64.8	0.3
70PG15R AP	22.1	30.7	45.3	1.9	77.9	41.8	8.3	58.2	0.6
70PG5P1 5RAP	23.5	30.3	43.5	2.7	76.5	46.4	5.5	53.7	0.5
70PG5PH G15RAP	29.8	28.4	36.9	5.0	70.3	44.7	5.1	55.4	0.4
52PG5P1 5RAP	22.9	29.8	44.1	3.2	77.1	33.2	4.0	66.8	0.3
70PG5P <sub>-</sub> B	22.4	25.5	47.2	5.0	77.7	41.6	5.2	58.4	0.5
70PG5P <sub>-</sub> B5SK	20.6	26.9	45.4	7.1	79.4	33.5	4.5	66.5	0.3
70PG5P <sub>-</sub> B10SK	22.2	25.2	47.3	5.2	77.7	42.1	3.2	57.9	0.3
70PG5P <sub>-</sub> B15SK	24.4	29.3	40.2	6.1	75.6	42.0	6.3	58.0	0.2

DEC ASPH = deconvoluted asphaltenes; HMW = high molecular weight;  
DEC MALT = deconvoluted maltenes; and J<sub>c</sub> = critical strain energy release rate.



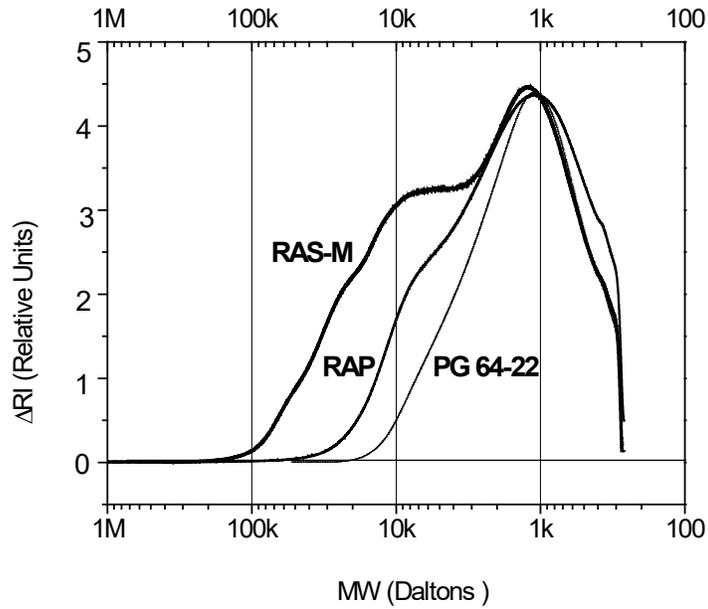
**Figure 15**

**Mixture critical strain energy rate vs. asphaltenes content (obtained from SARA fractionation)**

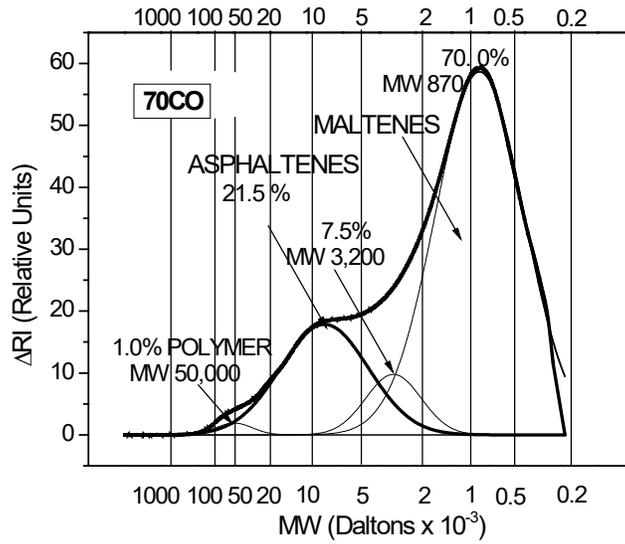
### Characterization of Asphalt Blends by GPC

The asphaltenes fraction is a critical component controlling the physical properties of the binder and the corresponding mixes. Asphaltenes are the bodying agent for the maltenes, which are simply a blend of low molecular weight aliphatic saturates. The largest "molecules" are assemblies of smaller monomer asphaltenes held together by one or more intermolecular forces. Through changes in the polarity of the solvent used in the analysis, the ability of the samples to undergo self-assembly by different interactive mechanisms has been probed [19]. Therefore, by analyzing the asphaltenes of asphalt paving combinations, such as asphalt cements and polymer-modified binders, with or without reclaimed asphalt materials (RAP, RAS), one might correlate physical performances of mixtures containing these materials with the content and MW magnitude of asphaltenes species [43]. RAS material can be generated from post-consumer (shingles that have been on roofs and have been removed), RAS-P, or manufactured waste (produced during manufacture of new shingles), RAS-M.

A large difference in MW distributions can be seen in GPC traces of samples of RAP, RAS-M and PG 64-22 binders (Figure 16). While the components of a PG 64-22 binder do not exceed MW 20K, and RAP MW 50K, the extremely large associations of the extracted RAS-M binder exhibit MW > 100K, i.e., in the domain of HMW polymers presented in Figure 17 for HMA mixture containing 0% RAS and PG70-22M binder.

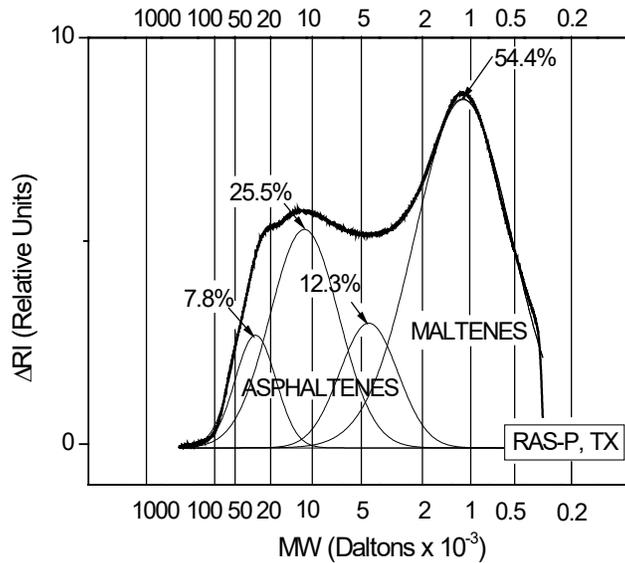


**Figure 16**  
**Typical molecular weight distribution of RAP, RAS and PG 64-22 binder**

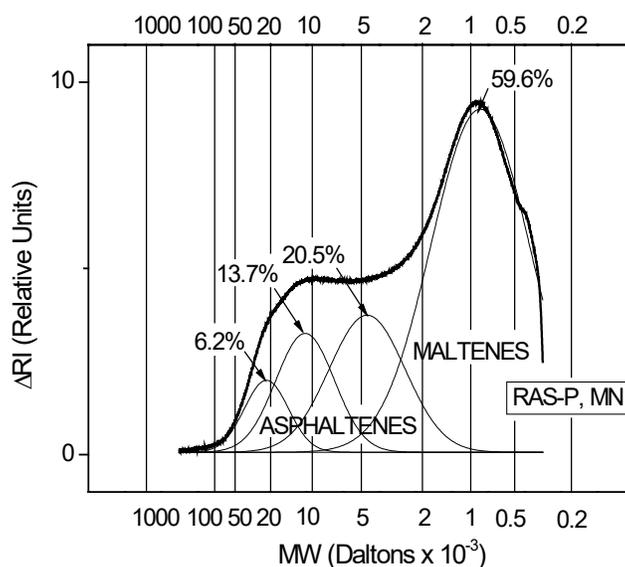


**Figure 17**  
**MW distribution of molecular species of extracted binder: PG70-22M binder (70CO)**

Asphalt binders extracted from RAS-M and post-consumer waste shingles (RAS-P) typically have different properties because of the aging of the latter that occurs after years of exposure on a roof. A further major concern with using recycled asphalt shingles relates to the variability in the properties of the RAS materials originating from different sources [34], [35]. While the GPC traces of extracted binders seem to be similar, discernible differences are evident when one compares the maltenes/high end asphaltenes (MW>10K Daltons) ratio of the extracts. This ratio identifies possible problems with compatibility of component species when blended with virgin asphalts (*vide infra*). For example, this ratio for the binder extracted from RAS-P originating from the Texan source, (Figure 18) is ~55/33, while for the Minnesota RAS-P extract presented in Figure 19, the maltenes/high end asphaltenes (MW>10K Daltons) ratio is quite different, viz., ~60/20.

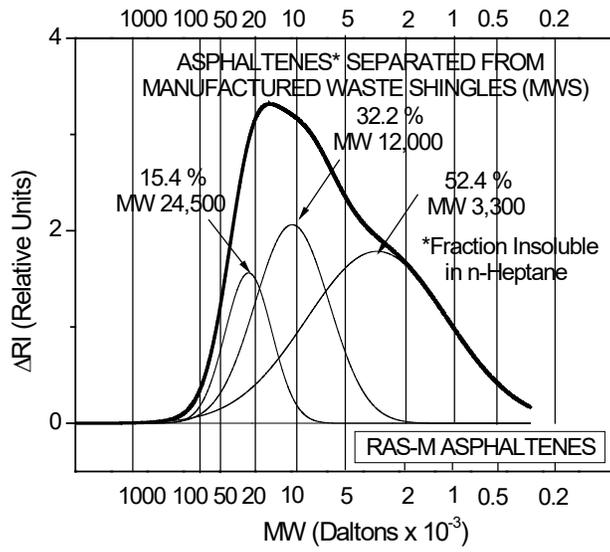


**Figure 18**  
**GPC traces of RAS binders extracted from RAS-P of Texas origin**

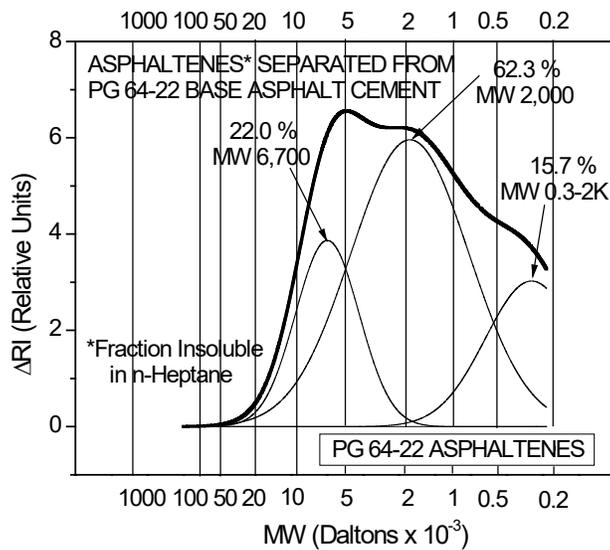


**Figure 19**  
**GPC traces of RAS binders extracted from RAS-P of Minnesota origin**

The asphaltenes fraction isolated by heptane precipitation of the asphalt binder isolated from a RAS-M sample was examined using GPC. The MW of molecular components of RAS-M (RAS-M) asphaltenes shown in Figure 20 surpasses greatly that of a similar precipitation of a PG 64-22 binder in Figure 21. Asphaltenes from PG 64-22 can be separated into two fractions. i.e., molecules with average MW 2,000 Daltons (62%) and associated asphaltenes with a peak average molecular weight of 6,700 Daltons (22%). The asphaltenes from RAS-M could be separated into three fractions with average MW's >3,000 Daltons (52%), 12,000 Daltons (32%) and 15% 24,500 Daltons (15%). Thus, associated asphaltenes with molecular weights higher than the associated asphaltenes in PG 64-22 comprise 47% of the RAS-M sample.

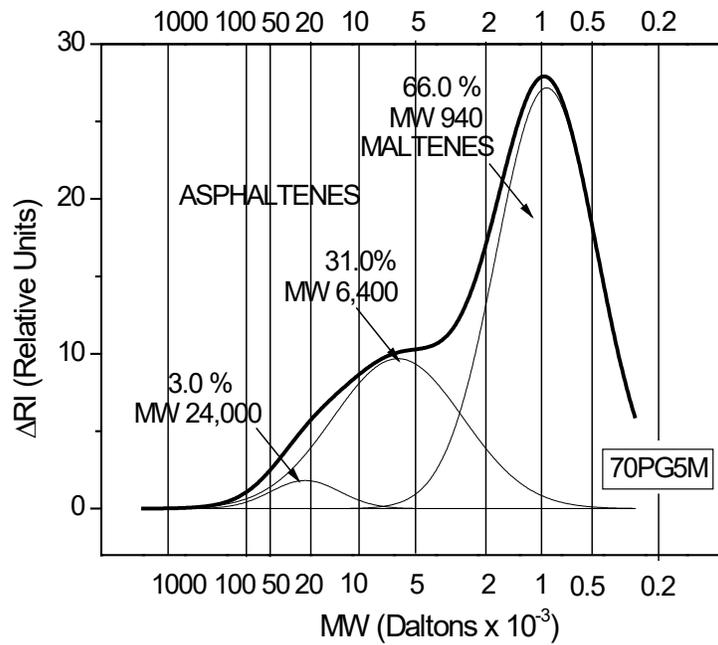


**Figure 20**  
**Average MW distributions of n-heptane insoluble asphaltenes species isolated from manufactured waste shingles (RAS-M)**

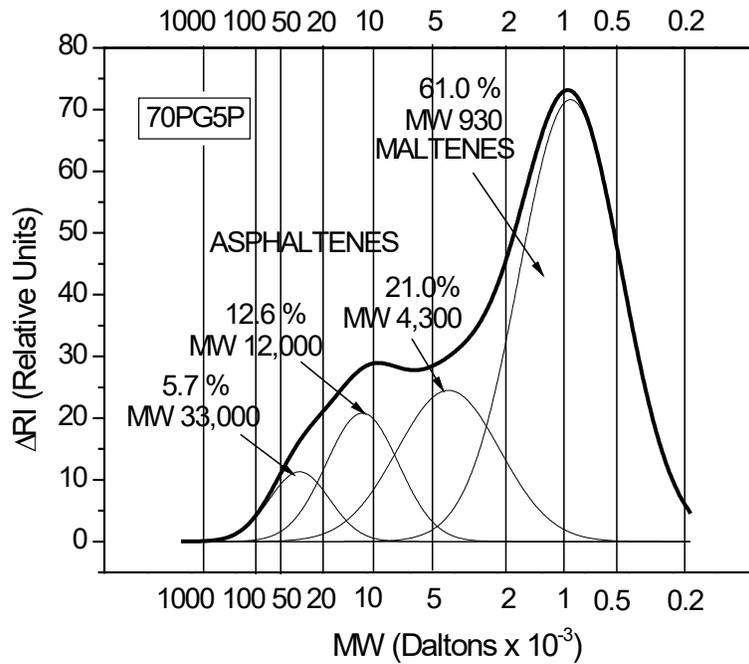


**Figure 21**  
**Average MW distributions of n-heptane insoluble asphaltenes species isolated from the PG-64-22 binder**

The GPC chromatograms in asphalt binder extracted from PG 70-22M and a binder mixture containing 5% RAS-P (70PG5P) presented in Figures 22 and 23, respectively. The contribution of extremely oxidized components in post-consumer waste shingles, RAS-P is apparent in Figure 23: the 70PG5P contains over 18% species with average MW>10K Daltons, out of which ~ 6% are of MW's averaging 33,000. In contrast, a mixture prepared with 5% RAS-M, 70PG5M, contained only 3% of species with average MW's of 24,000 Daltons. The maltenes/high end asphaltenes (MW>10K Daltons) ratio of 70PG5M (66/3) is significantly different from that of 70PG5P (61/18), suggesting a higher potential compatibility of mixtures containing RAS-M.



**Figure 22**  
**MW distribution of molecular species of 70PG5M binder extracted from PG 70-22M containing 5% RAS-M**

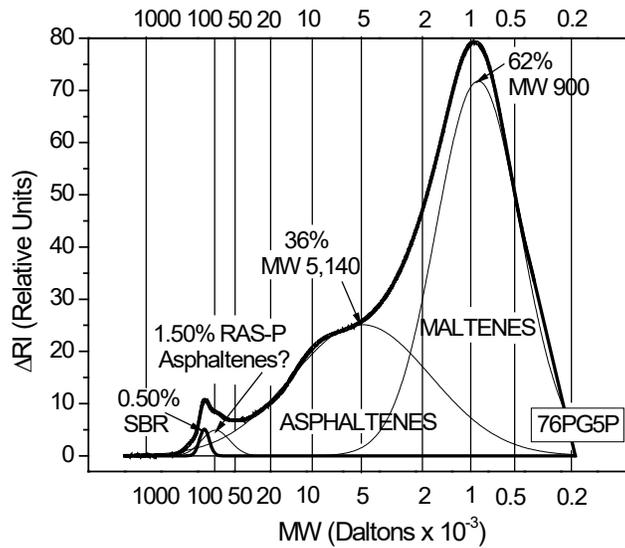


**Figure 23**

**MW distribution of molecular species of 70PG5P binder extracted from PG 70-22M containing 5% RAS-P**

The high MW end of associated RAS asphaltenes can exceed 100,000 Daltons, as depicted in Figure 24, the de-convoluted GPC chromatogram of 76PG5P binder obtained from PG 76-22M asphalt and 5% RAS-P. Both the residual polymer species (SBR) from the binder (0.5%) and the highest average MW asphaltenes species of RAS-P (1.5%) can be identified. The presence of the SBR polymer in the mix enhances the compatibility of the highly associated asphaltenes. However, the pattern of this RAS containing binder differs completely from that of 70PG5M and 70PG5P presented in Figures 22 and 23, respectively.

In Figure 24, the main asphaltenes peak, with a broad MW distribution, appears at around 5K Daltons, much lower than the average MW of associated RAS asphaltenes present observed in Figure 20. Apparently, the presence of  $\text{Ca}^{2+}$  ions from hydrated lime effected a redistribution of binder asphaltenes because the polar interactions, including hydrogen bonding, possibly because the ionic species disrupted the self-assembly among asphaltenes molecules [19].



**Figure 24**

**MW distribution of molecular species of 76PG5P binder (5.6% PG 76-22M, 5% RAS-P, 3% Hydrated Lime)**

The extremely large differences between the molecular weight distributions of associated asphaltenes found in RAS and those from base binders impacts the compatibility of the mixes when shingles are incorporated in paving asphalt materials. It has been reported that some blending occurred between virgin AC 64-22 binder and RAS binder during the HMA mixing and curing (or short-term aging) processes [13]. But the blending was not 100% since the high-temperature grades of the RAS-M and the RAS-P extracted binders, RAS-M and RAS-P, were 122°C and 166°C, respectively. The mixing temperature for a PG 64-22 binder is around 143°C (290°F) which was not high enough to blend RAS. Much higher blending temperatures are therefore required in order to make the RAS binder flow and comingle with virgin binder. Moreover, earlier investigations on cross-blending of asphaltenes and maltenes fractions among several asphalts indicated that the asphaltene fractions are not as equally interchangeable as are the maltene components, and that the effect of both molecular weight and the chemical nature of the asphaltenes must be taken into account to predict properties of asphalts from chemical composition [51]. Two types of segregation causing phase separations can occur when blending of asphalts containing dissimilar asphaltenes and maltenes fractions: one is simply separation as occurs in supersaturated solutions when components are ejected because of insufficient solvent (e.g., flocculation in blends of high

asphaltenes content); the other is rejection of a component when its amount exceeds the mutual compatibility limit, in the form of physical ejection of a liquid from a gel [18], [51].

In order to determine the compatibility of asphaltenes fractions from RAP and RAS, in blends containing only the asphaltenes precipitated from these asphalt materials as presented above, different blend compositions of RAP and RAS asphaltenes were prepared and analyzed by GPC. The results are presented in Table 5.

**Table 5**  
**Analysis of synthetic blends of RAS and RAP binders**

<b>Blend RAS:RAP Ratio %</b>	<b>Blending Composition %</b>	<b>Observed GPC Composition %</b>
<b>RAP 100%</b>		
<b>Polymer</b>		1.71
<b>Asphaltenes</b>		25.32
<b>Maltenes</b>		72.97
<b>RAS 100%</b>		
<b>Polymer</b>		15.56
<b>Asphaltenes</b>		32.04
<b>Maltenes</b>		52.40
<b>81:19 (RAP:RAS)</b>		
<b>Polymer</b>	4.33	7.25
<b>Asphaltenes</b>	26.60	30.28
<b>Maltenes</b>	69.07	61.47
<b>63:37 (RAP:RAS)</b>		
<b>Polymer</b>	6.83	6.31
<b>Asphaltenes</b>	27.81	29.80
<b>Maltenes</b>	65.36	63.89
<b>50:50 (RAP:RAS)</b>		
<b>Polymer</b>	8.64	4.13
<b>Asphaltenes</b>	28.68	28.27
<b>Maltenes</b>	62.68	67.60
<b>14:86 (RAP:RAS)</b>		
<b>Polymer</b>	10.43	11.56
<b>Asphaltenes</b>	29.56	32.54
<b>Maltenes</b>	60.00	55.90

The blending composition corresponds to the theoretical RAP:RAS ratio, while the actual GPC composition was determined by integration of GPC curves. For example, the blended amount of asphaltenes from the 81:19 blends, viz., 26.60%, was given by  $0.81 \times 25.32 +$

0.19x32.04. It should be compared to the larger actual GPC asphaltene composition of 30.28%. Perusing the other data of this table, one may conclude that there is, indeed, an interaction between RAP and RAS asphaltene, with unexpected results, such that of the 86:14 blends in which the actual GPC asphaltene composition (32.54%) seems to exceed that of 100% RAS (32.04%). These “new” asphaltene might result from the association of RAP low MW asphaltene fractions (<3,000 Daltons) overlapping the high MW end of maltenes, calculated as % maltenes.

In view of these observations, the large difference between the MW of asphaltene fractions of the base AC 64-22 (ca. 20% of maximum MW  $\approx$  7-8,000) and the asphaltene present in waste shingles (RAS M and P),  $\sim$  40% of MW >12,000, with 15% MW  $\approx$  25-30,000 Daltons) impacts the dispersion of large RAS asphaltene associations by the maltenes of the base asphalt with which the shingles will be blended. To this aim, one has to consider also the maltenes/high end asphaltene (MW>10K Daltons) ratio mentioned above: the higher the ratio, the better. It has been shown earlier that an increase in the binder content of LMW (i.e., MW<3K), or in other words of the content ratio of maltene/asphaltene, resulted in an increase in its elongation properties at intermediate and low temperatures [52].

#### **Determination of Carbonyl Index from FTIR Spectra of Asphalts**

In previous investigations related to aging of SBS copolymer modified asphalt cements, researchers have used FTIR in order to gain a relative understanding of oxidation, which is directly related to asphalt binder aging [48]. It was observed that the area of the carbonyl absorbance occurring at  $1700\text{ cm}^{-1}$  increased as compared to that of the C-C absorbance occurring at  $1455\text{ cm}^{-1}$ . The ratio of the C=O and C-C vibrations gave a relative comparison of how much oxidation is occurring. It was called carbonyl index. As the carbonyl (CO) index increased there was a higher level of oxidation in the asphalt binder and a stiffening of the binder has been observed [36]. Since both RAS-M and RAS-P are highly oxidized materials, it is expected that the carbonyl indices of paving asphalts incorporating RAS-M and RAS-P to be large. A correlation of CO index and the size and distribution of asphaltene given by the maltene/high end asphaltene (MW>10K Daltons) ratio might be attempted, to a limited extent, to predict the field performance at intermediate temperatures as reflected by the value of  $J_c$  integral. The carbonyl index for each sample discussed in this paper is reported in Tables 6-8.

**Table 6**  
**Stiffness of mixtures and carbonyl index of related RAS binders**

Run No.	Designation	Binder	RAS-P %	RAS-M %	Total MW >20K %	C=O Index X10 <sup>3</sup>	J <sub>c</sub> KJ/m <sup>2</sup>
21	70C0	PG70-22M	0	0	1.0	6.8	0.50
20	70PG5M	PG70-22M	0	5	3.1	12.0	0.50
16	70PG5P	PG70-22M	5	0	5.7	21.2	0.40
31	PG64-22	PG64-22	0	0	1.0	5.9	0.37
18	76CO	PG76-22M	0	0	1.3	10.2	0.60
17	76PG5P	PG76-22M	5	0	2.0	3.7*	0.75
33	SMACO	PG76-22M	0	0	6.2	8.1	0.72
34	SMA5P	PG76-22M	5	0	8.4	8.8	0.63

\*Presence of lime interferes with analysis

### Intermediate Temperature Cracking Performance of Asphalt Mixtures Containing Recycled Asphalt Shingles (RAS)

Since the asphaltene content in asphalts is related to the stiffness, the question arises: When blending virgin asphalt cement with RAS, will the asphaltene content of the resulting binder follow the additive rule and the J<sub>c</sub> will change correspondingly? The answer was NO in most cases because the non-polar maltenes of the virgin asphalt are not compatible with very highly oxidized RAS asphaltene species. It has been shown that the virgin/RAS binder blending was nonlinear, unlike the well-known virgin-RAP binder linear blending [2]. Postconsumer waste shingles (RAS-P) binders were much stiffer than manufactured waste shingles, RAS-M binders [13, 17]. Compared with RAS-P, RAS-M binders had much less impact on properties of blended virgin/RAS binders [9, 53]. Cooper reported that the addition of 5% postconsumer waste RAS-P decreased the intermediate temperature cracking resistance (expressed by critical strain energy J<sub>c</sub>) of a PG 70-22M binder when compared to

that of a similar mixture in which RAS-P has been substituted with manufactured waste RAS-M [53].

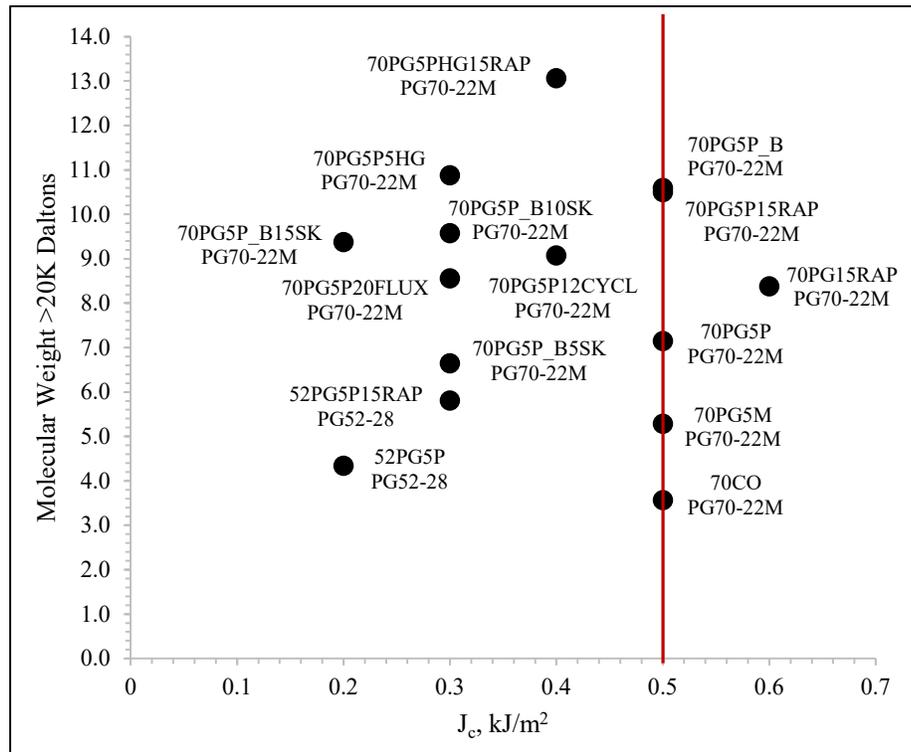
Analyzing the GPC data obtained for the same materials investigated by Cooper et al., i.e., 70PG5M and 70PG5P presented in Figures 22 and 23, respectively, we consider that the main reason for higher stiffness of the 70PG5P RAS-P binder reported by the authors is the degree of association of its large MW end asphaltenes ( $\sim 6\%$  of MW 33,000), which is higher than that found in the 70PG5M binder containing 5% RAS-M (3% MW 24,000 Daltons). It has been pointed out before that the ability of asphalts to form an intermolecular network by associations could lead to cracking with time and under cold conditions [19].

Table 6 contains the data for a series of asphalt binders extracted from RAS containing mixtures investigated in this work. The total percent content of asphaltenes with MW larger than 20K Daltons is listed together with the values of carbonyl index and of  $J_c$  integral in order to find a correlation between these data to predict, to a limited extent, the field performance of considered mixtures.

In Tables 6-9 advantage was taken of the ability to deconvolute the GPC curves to separate the associated asphaltenes fractions. Asphaltenes in virgin binders fall typically in the molecular weight range between 3 and 19K Daltons. Since the molecular weight of a monomeric asphaltenes molecule is estimated to be  $\sim 1000$  Daltons, some degree of association is observed even in virgin asphalts. However, when the molecular weight averages exceed 20K Daltons, these aggregated asphaltenes can be considered polymers. We have divided the asphaltenes polymers into two ranges, medium molecular weight associates (19K-45K Daltons) and high molecular weight associated asphaltenes with molecular weights from 45K up to 100K Daltons. The latter fraction overlaps the molecular weights observed for the elastomeric polymer addition such as SBS or SBR, the high molecular weight associated asphaltenes behave as brittle materials and tend to phase separate from the asphalt dispersion. This leads to poor cracking resistance as indicated by values of  $J_c$  significantly below the minimum threshold  $J_c$  value of  $0.5 \text{ kJ/m}^2$  being considered in Louisiana as an acceptance criterion.

A comparison of the critical strain energy ( $J_c$ ) data for mixtures evaluated in this study is presented in Figure 25 and Tables 6-8 versus the content of asphalt species with MW larger than 20K Daltons, the MW threshold of asphaltenes related to the stiffness of asphalt binders [54]. Higher  $J_c$  values are desirable for fracture-resistant mixtures. A minimum  $J_c$  value of  $0.50$  to  $0.65 \text{ kJ/m}^2$  is typically used as a failure criterion [44]. Data listed in Table 6 show that rather large carbonyl indices and low  $J_c$  values, less than the minimum Louisiana

acceptance of  $0.5 \text{ kJ/m}^2$ , were registered for mixtures containing PG 64-22 and PG 70-22 binders in which 3-6% asphalt species had  $\text{MW} > 20\text{K}$  (asphaltenes). However, the PG 76-22 mixtures containing sufficient polymers to accommodate RAS retained satisfactory  $J_c$ 's of at least  $0.6 \text{ kJ/m}^2$ . The presence of just 0.5% high MW polymer in 76PG5P can successfully prevent the stiffening effect of 1.5% high end large asphaltenes shown in Figure 24.



**Figure 25**

**Comparison of  $J_c$  values versus the content of asphalt fractions with  $\text{MW} > 20\text{K}$  Daltons**

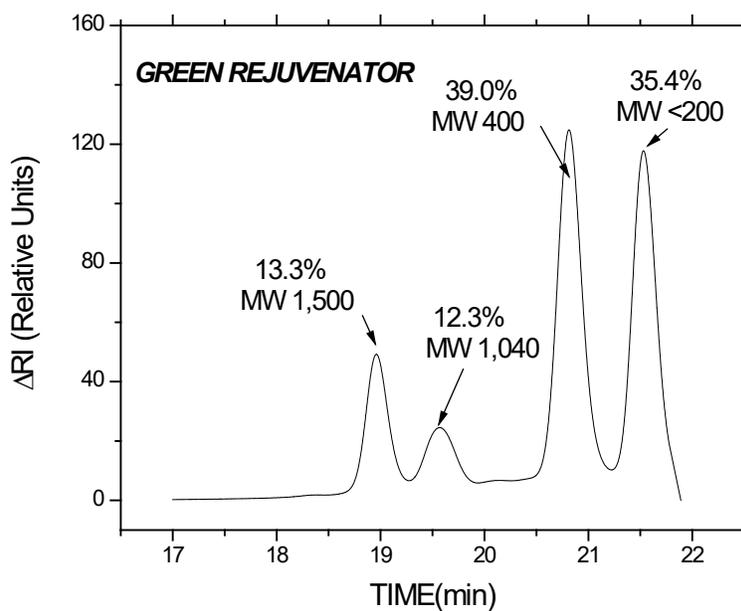
A correlation might be found between the GPC distribution of molecular weight of binders and of their polarity as expressed by the oxygen content (carbonyl index, CO) and the intermediate temperature performance (expressed by  $J_c$ ). High MW elastic polymers can be used to mitigate the stiffness of the resultant binder in RAS-P mixtures. A similar conclusion has been drawn for mixtures prepared with polymer-modified binders which were the best performers with straight unmodified binder [34].

## **Intermediate Temperature Cracking Performance of Asphalt Mixtures Containing RAS and Rejuvenating Agents**

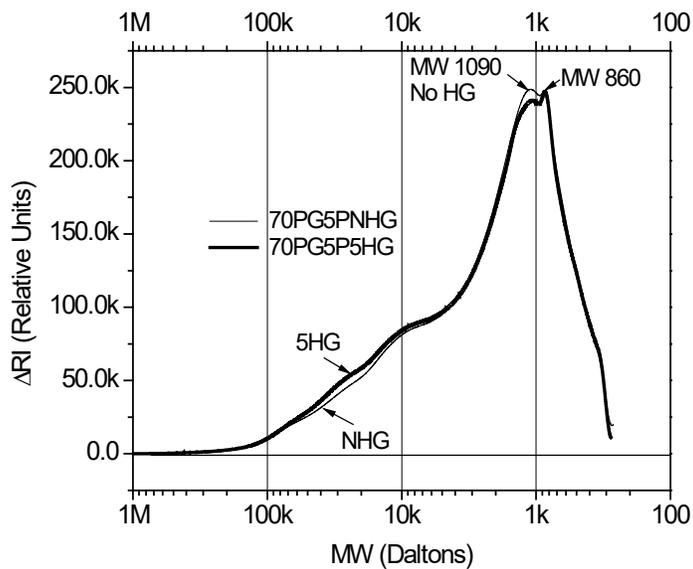
The recycling agents (RA) considered in this project are promoted as rejuvenators and/or softeners. The rejuvenating agents include: lube extracts; extender oils (Hydrolene aromatic oils) (RA-7); anti-stripping agent naphthenic oil (Cyclogen-L, RA-3), vegetable derived oils (RA-2), Reclaimate base oil (RA-5) and medium neutral oil (RA-6). Rejuvenators are designed to restore the physical and chemical properties of aged binder that has lost its maltenes during construction and service. They contain a high proportion of maltene constituents, and naphthenic or polar aromatic fractions. The following materials have been used as softeners in this project: asphalt flux oils (RA-4), soft asphalt binders (RA-1) and recycled engine oil bottoms (RA-8). The GPC MWD's and carbonyl indexes of the recycling agents are compiled in Table 1.

As shown in Table 1, RAS contain highly associated asphaltenes with apparent molecular weights approaching 100K. The rejection of high MW RAS components ( $MW > 20K$ , see Figures 16 and 17) when its amount exceeds the mutual compatibility limit with added virgin asphalt may be the main cause for the drop in stiffness for the RAS mixtures investigated by Mogaver et al. and low cracking resistance of RAS-P containing binders when polymers are not present as shown in Figure 24 [55]. Association should be reduced by adding rejuvenators in order to improve the intermediate temperature performance (expressed by critical strain energy,  $J_c$ ).

As indicated above, vegetable derived oil (RA-2), Hydrogreen (HG), was one of the recycling agents chosen for the present study. Hydrogreen is an esterified derivative obtained from rosin, a by-product of the pulp and paper industry. This environmentally green rejuvenator is a low molecular product with the MW distribution shown in Figure 26. Its oxygen content is reflected by a significant carbonyl index ( $CO = 0.04$ ). Only 25% of its species matches the molecular weight of maltenes from an asphalt binder ( $MW \approx 800-1500$ ). The anticipated role of the rejuvenators for RAS mixtures is to lower the association of high-end large MW asphaltenes present in RAS binders – a hard nut to crack. However, addition of 5% HG to a PG 70-22 binder containing 5% RAS-P (#50 70PG5P5HG) does not seem to affect the distribution of high MW fractions derived from RAS-P (Figure 26). In fact, the data in Table 8 show that the concentration of associated asphaltenes with molecular weights between 19-45 K and 45-300 K actually increases. Researchers at LTRC have estimated that RA-2 promotes the extraction of the binder from the RAS-P so this increase could be due to the extraction of high molecular weight associated asphaltenes.



**Figure 26**  
**Molecular mass distribution of R2 green rejuvenator**

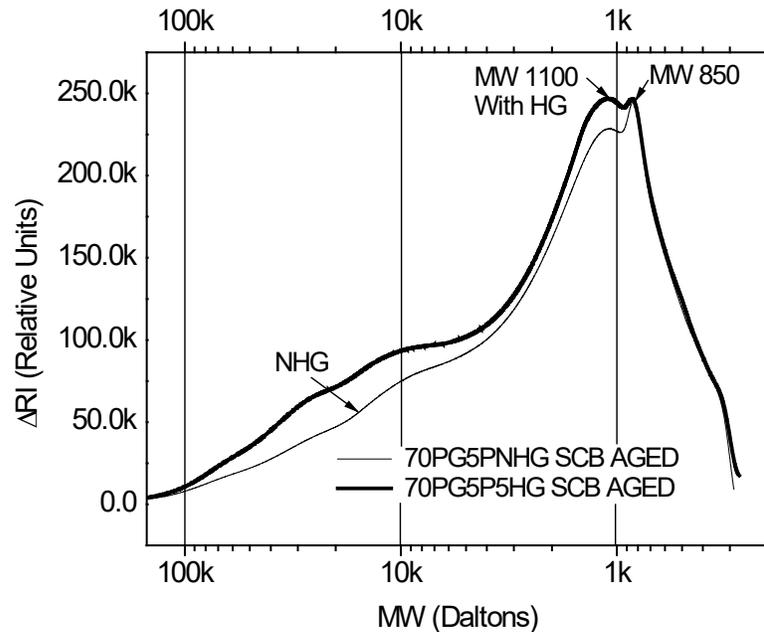


**Figure 27**  
**GPC traces of PG 70-22M containing 5% RAS-P with (70PG5P5HG) or without (70PG5P5NHG) 5% HGR by total weight of mix**

At the same time, data listed in Table 7 and Figure 27 show that the addition of 5% RA-2 to a PC 70-22 binder containing 5% RAS-P (#50 70PG5P5HG) did not eliminate the high MW asphaltenes and did not preclude the increase of this fraction by aging of the mixture for 5 days at 85°C (SCB aging). It even seems that this rejuvenator promotes aging. The increase of asphaltenes from 9.6% to 11.5% and the corresponding reduction of the content of maltenes is associated with a the decrease of  $J_c$  from 0.37 to 0.26 kJ/m<sup>2</sup>.

**Table 7**  
**Stiffness of mixtures and carbonyl index of related RAS binders containing recycling agents**

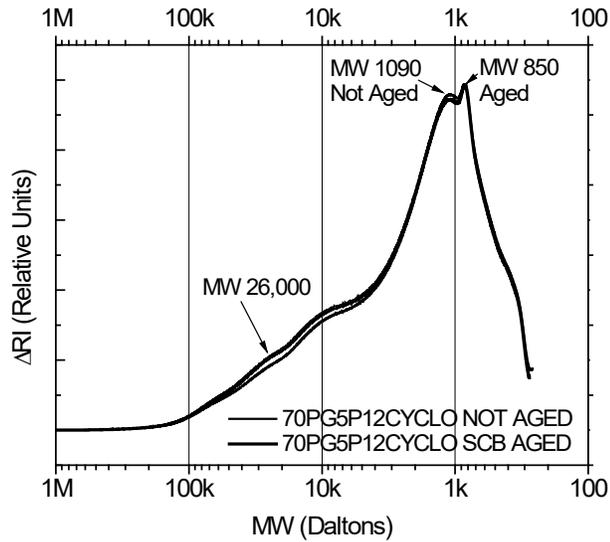
<b>Sample ID</b>	<b>Total VHMW % Polymer &amp; Highly Associated Asphaltenes 1000K-19K</b>	<b>Total HMW % (Asphaltenes) 19K-3K</b>	<b>Maltenes % &lt; 3K</b>	<b>C=O Index x10<sup>3</sup></b>	<b>J<sub>c</sub> KJ/m<sup>2</sup></b>
<b>70PG5P5HG AGED 5days @85C:</b>	9.59	28.06	62.34	13.9	0.37
	11.50	29.06	59.43	17.1	0.26
<b>70PG5P12CYCL AGED 5days @85C</b>	8.30	25.98	65.38	9.9	0.13
	8.77	27.17	64.06	13.0	0.36
<b>70PG5P150PEN AGED 5days @85C</b>	4.62	24.78	70.59	9.1	0.17
	5.68	26.10	68.22	11.7	0.24



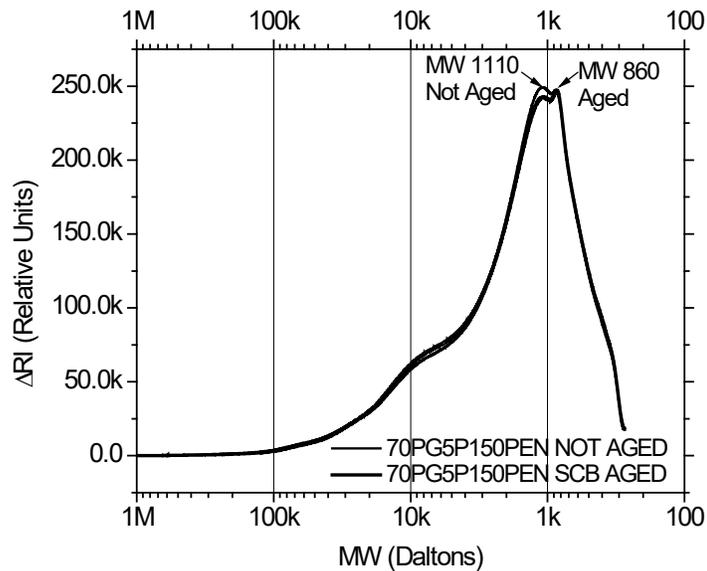
**Figure 28**

**GPC traces of SCB aged PG 70-22M containing 5% RAP-P with (70PG5P5HG) or without (70PG5P5NHG) 5% HGR by total weight of mix**

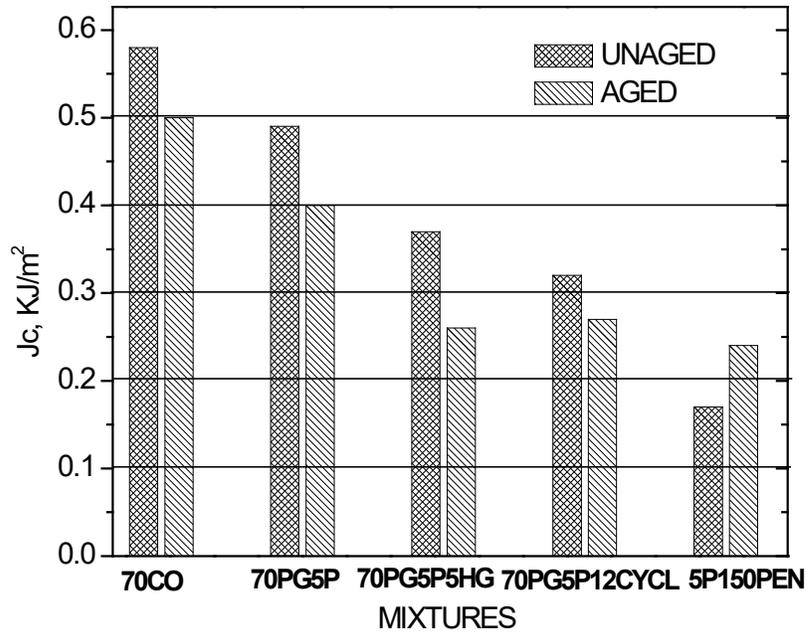
Blending and aging of 70PG/RAS-P binders with other rejuvenating agents thought to improve the low temperature performance of the mixtures provided similar results (Table 7). An asphalt cement meeting a PEN 150 (PG52-28) was used as a softening agent (RA-1). Adding softening agents did not seem to alter the MW distribution of asphalt components (Table 8). GPC traces and MW distribution remained practically the same after SCB aging of both Cyclogene (RA-3) and PG 58-22 (PEN 150) containing PG 70-22M binders (Figures 29 and 30). While CO index increased accordingly after aging, the cracking resistance expressed by critical strain energy,  $J_c$ , remained below the accepted limit ( $J_c < 0.5 \text{ kJ/m}^2$ ), with decreased values for SCB aged mixtures (Figure 31).



**Figure 29**  
**GPC traces of SCB aged and un-aged PG 70-22M containing 5% RAS-P with 12% RA-3 by total weight of mix**



**Figure 30**  
**GPC traces of SCB aged and un-aged PG 70-22M containing 5% RAS-P with 4.6% RA-1 by total weight of mix**



**Figure 31**  
 **$J_c$  versus asphalt mixture types before and after aging**

The authors concluded at this stage of the project that both RAS-M and RAS-P are much more highly oxidized than RAP as indicated by FTIR spectroscopy. The concentration of RAS asphaltenes exceeds 40 wt.% of which 25 wt. % are highly aggregated with apparent molecular weights approaching 100K. Mixes with a high content of AC species with MW > 20K (associated asphaltenes) are relatively brittle. The poor intermediate temperature performance is predicted by  $J_c$  integrals < 0.5 kJ/m<sup>2</sup>.

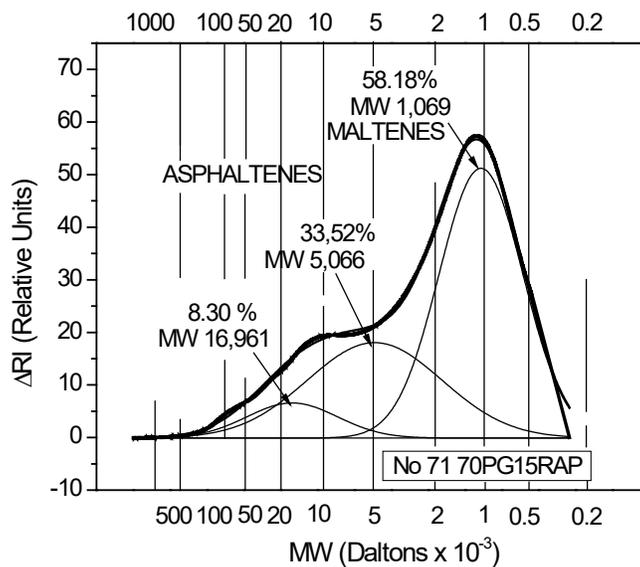
The high molecular weight associated asphaltenes are not significantly dissociated by adding rejuvenators to either RAP-M or RAP-P containing mixes. The rejuvenators negatively impact intermediate temperature performance.

**Table 8**  
**Impact of hydrogreen recycling agent in RAP and RAS/RAP asphalt blends**

Mix Designation	Binder	% Binder	%RAS	%RAP	% Rejuvenator	1000K- 300K	300k-45K	45K-19K	Total high MW (1000K-19K)	19K-3K (asphaltenes)	<3k (Maltenes)	Carbonyl index	J <sub>c</sub>
RAP RAS 64-22	PG 64-22	5.6	0.6	0.9		0.22	7.13	2.5	<b>9.89</b>	<b>31.38</b>	<b>58.73</b>	<b>0.1124</b>	<b>0.48</b>
RAP RAS 64-22 HG	PG 64-22	5.4	0.6	0.9	5	0.16	0.85	2.53	<b>3.54</b>	<b>27.47</b>	<b>68.99</b>	<b>0.10641</b>	<b>0.26</b>
RAP RAS 58-28	PG58-28	5.4	0.6	0.9		0.15	1.07	3.57	<b>4.79</b>	<b>28.52</b>	<b>66.69</b>	<b>0.1111</b>	<b>0.25</b>
RAP RAS 64-22 HG	PG58-28	5.4	0.6	0.9	5	0.18	1.13	4.26	<b>5.57</b>	<b>28.96</b>	<b>65.47</b>	<b>0.1256</b>	<b>0.21</b>
RAP RAS 64-22	PG 64-22	5.2	0.6	0.9		0.04	1.41	5	<b>6.45</b>	<b>29.18</b>	<b>64.37</b>	<b>0.1606</b>	<b>0.31</b>
RAP RAS 64-22 HG	PG 64-22	5.2	0.6	0.9	5	0.01	0.41	1.9	<b>2.32</b>	<b>26.8</b>	<b>70.88</b>	<b>0.1671</b>	<b>0.26</b>
RAP RAS 58-28	PG58-28	5.1	0.6	0.9		0.03	1.41	4.99	<b>6.43</b>	<b>29.19</b>	<b>64.38</b>	<b>0.2</b>	<b>0.31</b>
RAP RAS 64-22 HG	PG58-28	5.5	0.6	0.9	5	0.04	1	3.35	<b>4.39</b>	<b>27.4</b>	<b>68.2</b>	<b>0.0914</b>	<b>0.32</b>
70PG15RAP	PG70-22M	4.5	0	15		0.33	3.03	5.02	<b>8.38</b>	<b>28.26</b>	<b>63.36</b>	<b>0.095</b>	<b>0.55</b>
70PG5P15RAP	PG70-22M	4.1	5	15	0	0.24	3.26	7	<b>10.5</b>	<b>30.23</b>	<b>59.27</b>	<b>0.1406</b>	<b>0.46</b>
70PG5P5HG15RAP	PG70-22M	<b>3.1</b>	<b>5</b>	<b>15</b>	<b>5</b>	0.47	4.52	8.08	<b>13.07</b>	<b>29.84</b>	<b>57.09</b>	<b>0.212</b>	<b>0.42</b>
52PG5P15RAP	PG52-28	3.5	5	15	0				<b>5.81</b>	<b>28.56</b>	<b>65.63</b>	<b>0.01256</b>	<b>0.3</b>

## Characterization of Binders Extracted from Mixture Containing RAP, RAS and Recycling Agents

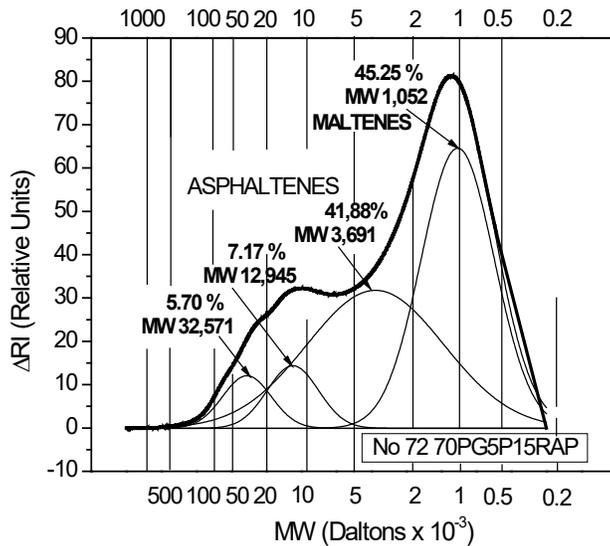
Louisiana RAP samples usually contain residual SBS polymer. This suggests that adding RAP to a mixture containing RAS-M or RAS-P would improve the potential compatibility of the tertiary mixes. The mixture design for the investigations presented in the following was characterized in terms of : RAS Type (RAS-P); % RAS Total AC Content (28.6); % RAS in Mix Design (5.0); % RAS AC Binder Available(1.4). The mixture content of the recycling agents (RAs) varied according to the recommendations of the vendors. The results are compiled in Table 9. Supposedly, the RAs should reduce the MW of large asphaltene associations to that of RAP containing binders, as presented in Figure 32, viz., max 8-10% of MW <20K Daltons ( $J_c = 0.6 \text{ kJ/m}^2$ ).



**Figure 32**

**MW distribution of molecular species of extracted binder: HMA mixture containing 15% RAP, 0% RAS and PG70-22M binder (70PG15RAP)**

Adding 5% RAS to the mixture containing 15% RAP resulted in a lower  $J_c$ , but within the limit of acceptability,  $J_c = 0.5 \text{ kJ/m}^2$ . Perhaps this strength is due to the effect of the additional polymer contained in the RAP binder. The GPC of the MW species of 70PG5P15RAP is presented in Figure 33. A percentage of ~6% MW species of 32-33K, typical for RAS association of asphaltenes, is present in the distribution of the extracted binder.

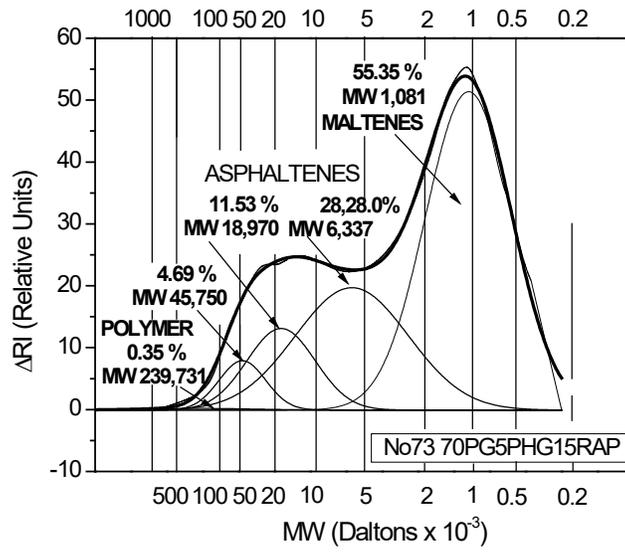


**Figure 33**

**MW distribution of molecular species of extracted binder: HMA mixture containing 15% RAP, 5% RAS and PG70-22M binder (70PG5P15RAP)**

However, none of the RA's considered in this project improved the cracking resistance, i.e., for each mixture with added RA the  $J_c < 0.5 \text{ kJ/m}^2$ . It should be mentioned that the 70PG5P mixture containing RAP presented in Figure 32 had a satisfactory  $J_c = 0.5 \text{ kJ/m}^2$ . However, the RAS containing mixtures, such as 70PG5P, contain only a fraction of the available RAS binder in the binder extract (36% in the case of 70PG5P). RA agents help to elevate the extraction of RAS binders up to 100%. The additional RAS binder extracts would have large RAS-M components which otherwise did not be extracted into the mixture (i.e., extracted and blended with the PG 70-20M binder).

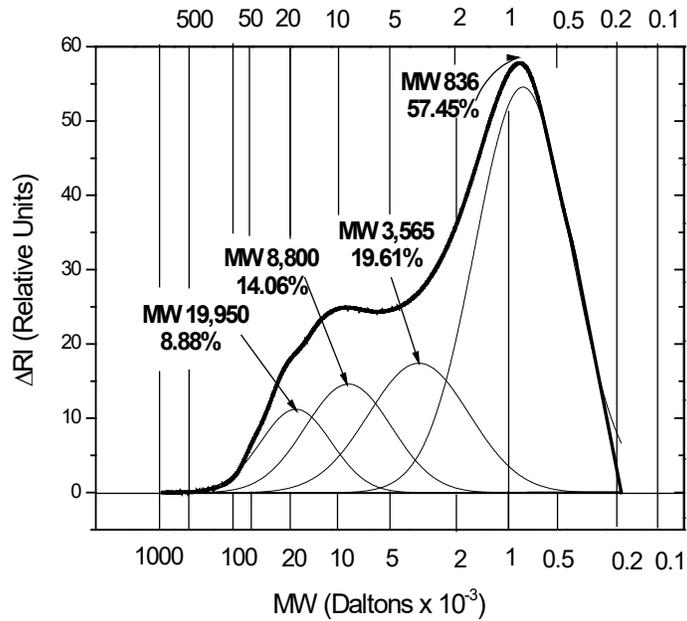
When the mixture has been prepared using the vegetable derived oil RA-2 agent (Hydrogreen),  $J_c$  dropped to  $0.3 \text{ kJ/m}^2$ . This result might be associated with the increase of the molecular weight (and size) of associated asphaltenes from  $\text{MW} \sim 30\text{K}$  to  $\text{MW} > 40\text{K}$  (Figure 34).



**Figure 34**

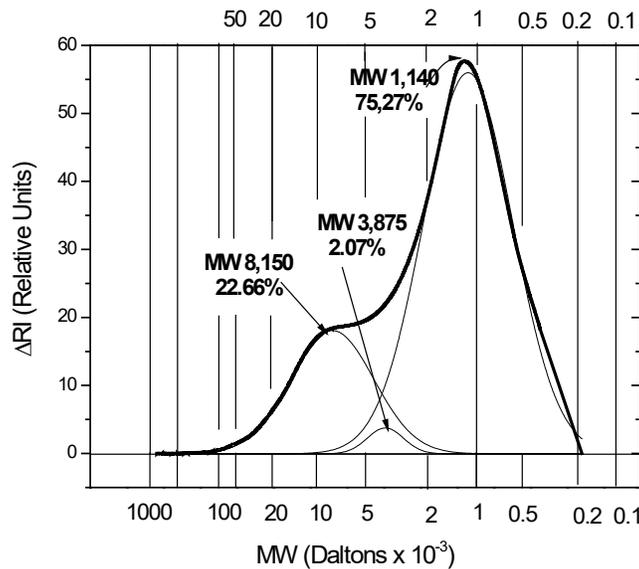
**MW distribution of molecular species of extracted binder: HMA mixture containing (0.75+5%) RA-2 (Hydrogreen), 15% RAP, 5% RAS and PG70-22M binder (70PG5PHG15RAP)**

A PG 64-22 mixture containing RAP and RAS had  $J_c = 0.48 \text{ kJ/m}^2$ , which dropped to  $J_c = 0.26 \text{ kJ/m}^2$  after RA-2 (Hydrogreen) has been added to the system (Figures 35 and Figure 36, respectively). Comparatively the MW of asphaltenes has been reduced (Figure 37), but the recycling agent RA-2 acted as a softener.



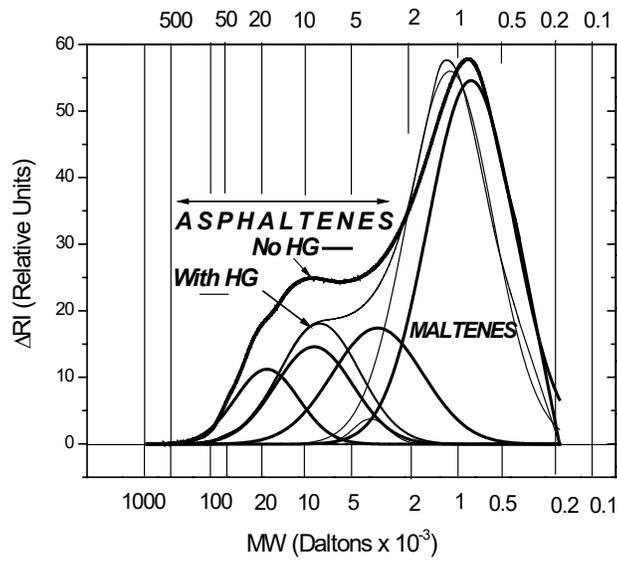
**Figure 35**

**Molecular weight distribution of No 3 RAP RAS 64-22 LL (5.6% PG 64-22 RAP AC = 0.9, RAS AC = 0.6, LL) J<sub>c</sub> 0.48**



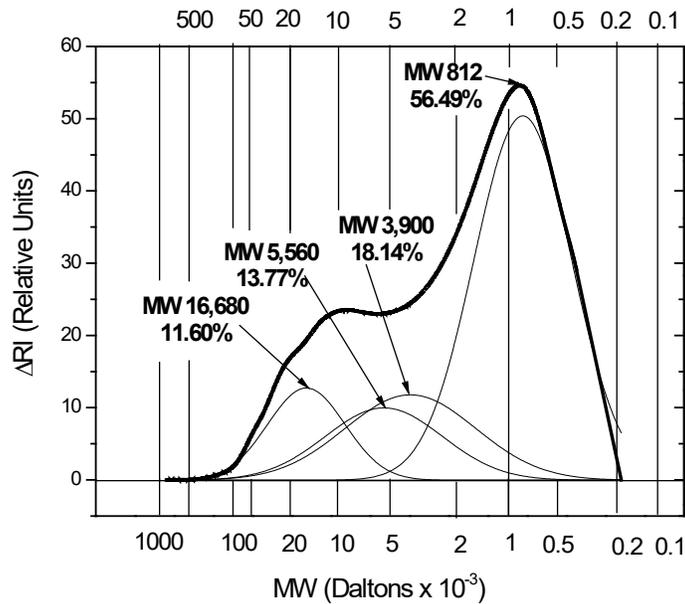
**Figure 36**

**Molecular weight distribution of No 4 RAP RAS 64-22 LL (5.6% PG 64-22 RAP AC = 0.9, RAS AC = 0.6, LL) with RA-2 (J<sub>c</sub> 0.26)**



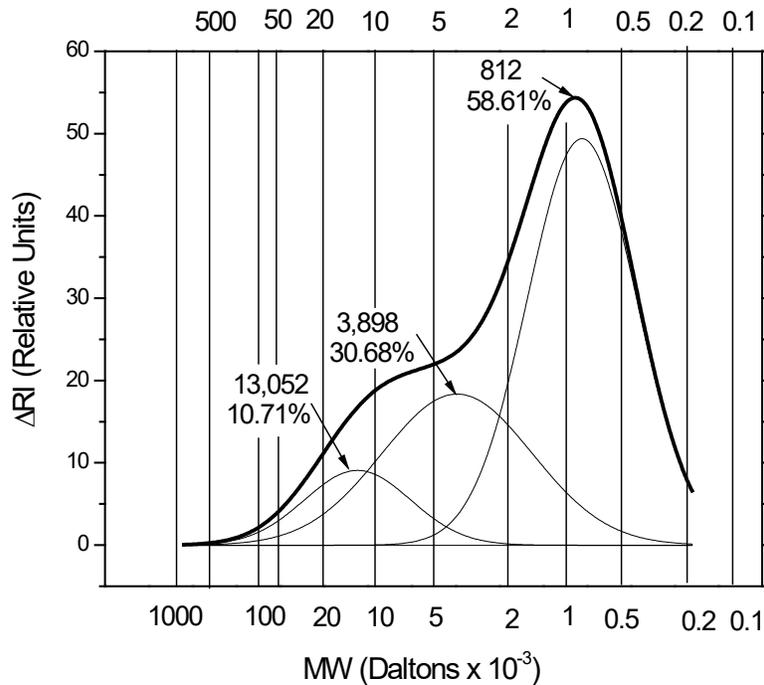
**Figure 37**

**Comparison between molecular weight distribution of RAP RAS 64-22 LL binders prepared with no HG (RA-2) or using HG (RA-2) recycling agent**



**Figure 38**

**Molecular weight distribution of No 3 RAP RAS 58-28 LL (5.6% PG 64-22 RAP AC = 0.9, RAS AC = 0.6, LL) Jc 0.25**

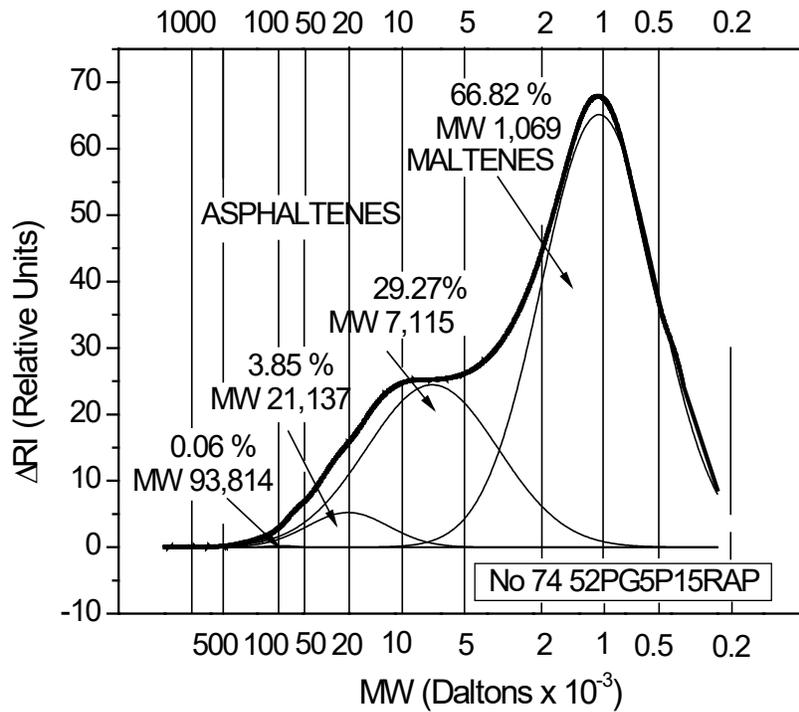


**Figure 39**

**Molecular weight distribution of No 4 RAP RAS 58-28 LL (5.6% PG 64-22 RAP AC = 0.9, RAS AC = 0.6, LL) with RA-2 ( $J_c$  0.21)**

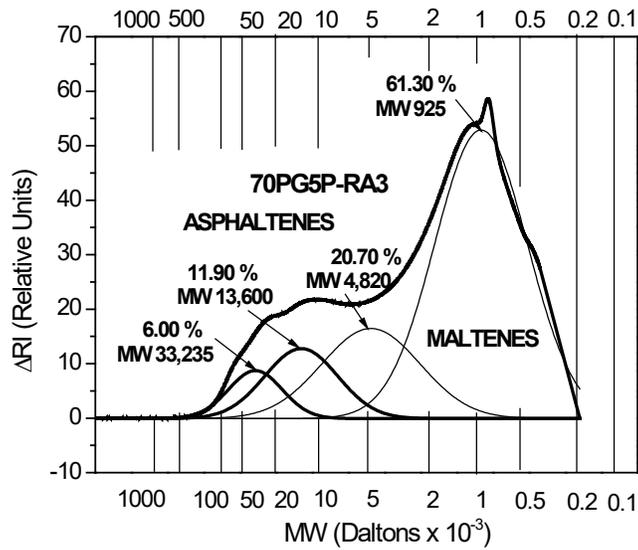
Similar results have been obtained when PG 64-22 binder was replaced with PG 58-28 asphalt. In these cases  $J_c$  dropped from  $J_c = 0.25$  kJ/m<sup>2</sup> to  $J_c = 0.21$  kJ/m<sup>2</sup> after RA-2 was added to the system (Figures 38 and 39).

Using only the softening agent RA-1 (Soft PG 52-28 Asphalt Binder), the large MW asphaltene association from RAS have not been extracted and therefore the low  $J_c = 0.2$  kJ/m<sup>2</sup> registered for the mixture was due only to the softening effect of maltene fractions (67% MW = 1K) and the small asphaltene content of moderate MW (3.85% MW 21K) (Figure 40).



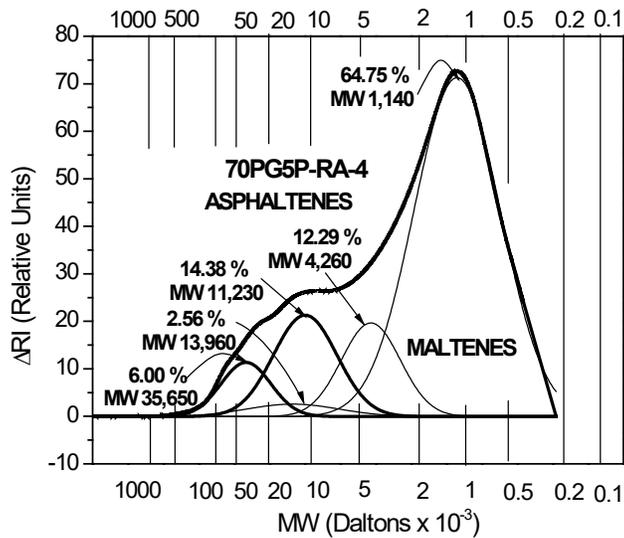
**Figure 40**  
**MW distribution of molecular species of extracted binder containing only RA-1:**  
**52PG5P15RAP ( $J_c$  0.2)**

The influence of RA-3 (12% Cyclogen-L, Naphthenic Oil) and RA-4 (20% Asphalt Flux, Softening Agent) is presented in Figures 41 and 42, respectively. In these cases  $J_c$  dropped from  $J_c = 0.5 \text{ kJ/m}^2$  (No RA added) to  $J_c = 0.4 \text{ kJ/m}^2$  (RA-3 added) and  $J_c = 0.3 \text{ kJ/m}^2$ , respectively (RA-4 added).



**Figure 41**

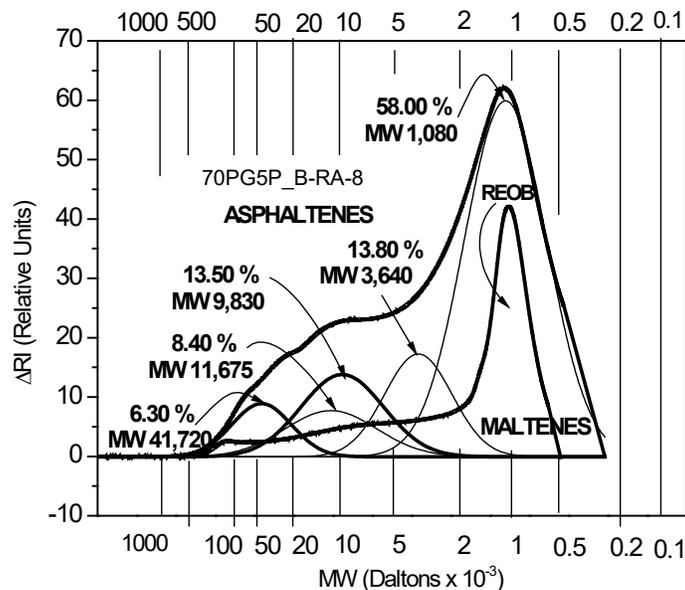
**MW distribution of molecular species of extracted binder: HMA mixture containing RA-3 (12% Cyclogen L, Naphthenic Oil), No RAP, 5% RAS and PG70-22M binder (Jc 0.4)**



**Figure 42**

**MW distribution of molecular species of extracted binder: HMA mixture containing RA-4 (20% Asphalt Flux, Softening Agent), No RAP, 5% RAS and PG70-22M binder (Jc 0.3)**

The last RA investigated was the SafetyKleen (RA-8, REOB) the bottom material remaining from recycled motor oil. The mixture (70PG5P\_B-RA8) contained 5% RAS and 15% REOB (Figure 43). However, in this case also the  $J_c$  was very low ( $J_c = 0.23 \text{ kJ/m}^2$ ).



**Figure 43**

**MW distribution of molecular species of extracted binder: HMA mixture containing 15% REOB (70PG5P\_B-RA8)**

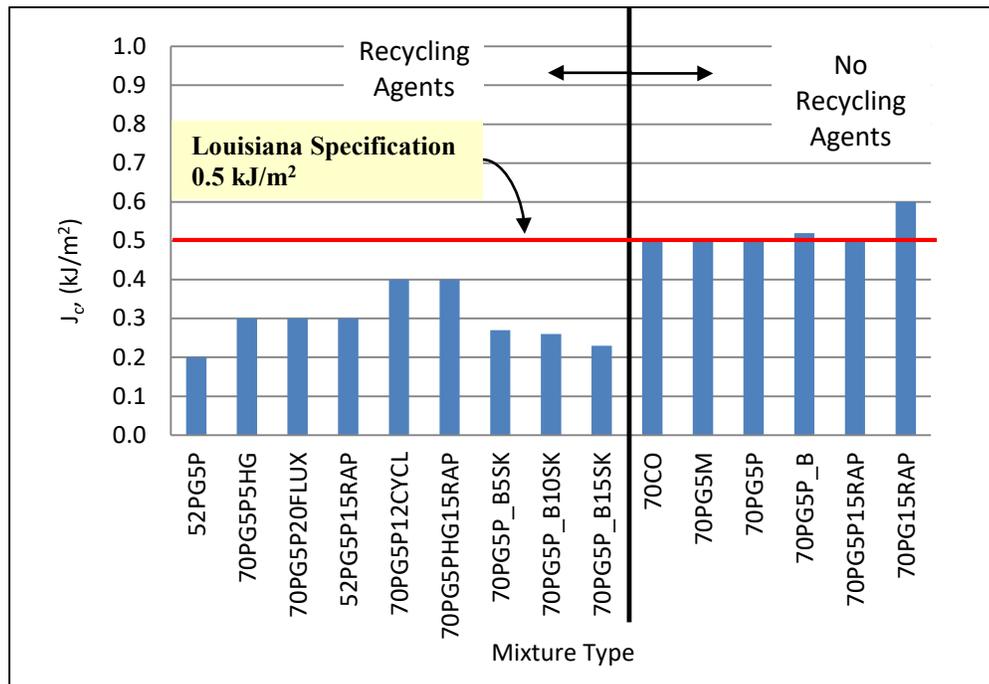
The use of re-refined engine oil bottoms (REOB) in paving mixtures as a rejuvenating agent was examined. A series of mixtures were prepared containing increasing amounts REOB (SafetyKleen, SK). Three dosages of REOB were considered in this study: 5-, 10-, and 15%, respectively. It should be mentioned that in these cases REOB did not displace the asphalt in binder compositions. REOB by itself has the distribution of molecular species of MW concentrated in the domain of asphalt maltenes, with a tail towards the species of HMW polymers (Figure 43). Mixture 70PG5P\_B5SK contained 5% RAS and 5% REOB, while mixtures 70PG5P\_B10SK and 70PG5P\_B15SK were prepared with 10% and 15% SK, respectively. It seems that REOB acts only as a diluting agent, with good capacity of extracting the RAS material. For example, the binder extracted from mixture

70PG5P\_B15SK contained all the asphalt binder present in RAS-P (100% RAS extraction; compare with 36% availability for mixture 70PG5P). Less RAS binder extraction was observed when the REOB addition to the mixtures dropped to 10% and 5%. However, the REOB content did not improve the cracking resistance;  $J_c$  remained below the threshold limit of  $0.5 \text{ kJ/m}^2$ , Table 9. The extracting power of REOB is reflected by the increase of the size of associated asphaltenes originating from RAS i.e. species exceeding  $\text{MW} > 40\text{K}$  Daltons. Illustrative data regarding the distribution by size and polarity of asphalt species composing the binders extracted from mixtures containing REOB are presented in Table 9 and Figure 43 (70PG5P\_B15SK). As previously shown, RAS asphaltenes are highly associated with apparent molecular weights approaching  $100\text{K}$  Daltons. The rejection of high MW RAS components ( $\text{MW} > 20\text{K}$  Daltons) when its amount exceeds the mutual compatibility limit with added virgin asphalt, may be the main cause for the drop in stiffness for the RAS mixtures investigated by Mogawer et al., and low cracking resistance of RAS-P containing binders when polymers are not present as shown in Figure 43 [55].

**Table 9**  
**GPC, carbonyl index and J<sub>c</sub> of RAP/RAS mixes**

<b>Mix Designation</b>	<b>% PG70-22M Binder</b>	<b>%RAS</b>	<b>Rejuvenator</b>	<b>% Rejuvenator</b>	<b>1000K- 300K</b>	<b>300k-45K</b>	<b>45K-19K</b>	<b>Total high MW (1000K-19K)</b>	<b>19K-3K (asphaltenes)</b>	<b>&lt;3k (Maltenes)</b>	<b>Carbonyl index</b>	<b>J<sub>c</sub></b>
70 CO-LL	5.3	0		0	0	1.09	2.48	<b>3.57</b>	<b>25</b>	<b>71.43</b>	0.0681	0.5
70PG5PNHG	3.9	5		0	0.15	2.55	5.36	<b>8.06</b>	<b>27.71</b>	<b>64.23</b>	0.1013	0.39
70PG5P5HG	3.9	5	RA-2	5	0.03	3.29	7.56	<b>10.88</b>	<b>29.05</b>	<b>60.07</b>	0.1713	0.23
70PG5P12CYC	3.9	5	RA-3	12	0.07	2.87	6.12	<b>9.08</b>	<b>27.35</b>	<b>63.57</b>	0.1305	0.36
70PG5P150AC	3.9	5	RA-1	4.6	0.09	1.15	3.1	<b>4.34</b>	<b>25.1</b>	<b>70.56</b>	0.1174	0.22
70PG5P7.5 Reclaimite	3.9	5	RA-5	7.5	0.09	3.28	6.32	<b>9.69</b>	<b>27.29</b>	<b>62.71</b>	0.1079	----
70PG5P5MNE	3.9	5	RA-6	5	0.14	4.59	7.79	<b>12.52</b>	<b>27.76</b>	<b>59.72</b>	0.092	----
70PG5P15Flux	3.9	5	RA-4	15	0.12	3.28	5.99	<b>9.39</b>	<b>28.13</b>	<b>62.48</b>	0.0803	----
70PG5P20Flux not aged	3.9	5	RA-4	20	0.16	3.04	6.23	<b>9.43</b>	<b>30.24</b>	<b>60.33</b>	0.1313	0.28
70PG5P20Flux	3.9	5	RA-4	20	0.33	3.36	5.02	<b>8.56</b>	<b>29.23</b>	<b>62.21</b>	0.1666	0.3
70PG5P7.5Hydro-lene	3.9	5	RA-7	7.5	0.06	2.6	5.17	<b>7.83</b>	<b>26.79</b>	<b>65.38</b>	0.1053	----
70PG5P_B15SK	4.3	5	REOB	15			6.3	<b>6.3</b>	<b>35.7</b>	<b>58</b>	0.1246	0.23
70 CO (STA)-Not Aged	5.3	0		0	0.19	2.13	3.41	<b>5.73</b>	<b>26.69</b>	<b>67.58</b>	0.0518	0.58
70PG5PCO (STA)-Not Aged	4.8	5		0	0.33	3.25	5.37	<b>8.95</b>	<b>28.01</b>	<b>63.04</b>	0.0964	0.49

Reducing asphaltenes' association by adding rejuvenators in order to improve the intermediate temperature performance (expressed by critical strain energy release rate,  $J_c$ ) failed. Blending and aging of 70PG/RAS-P binders with rejuvenating agents thought to improve the low temperature performance of the mixtures does not improve the medium temperature cracking resistance. Adding softening agents did not seem to alter the MW distribution of asphalt components (Table 9). The cracking resistance expressed by  $J_c$  remained below the accepted limit ( $J_c < 0.5 \text{ kJ/m}^2$ ) with decreased values for SCB aged mixtures. (Figure 44).



**Figure 44**  
**J<sub>c</sub> vs asphalt mixture types**



## CONCLUSIONS AND RECOMENDATIONS

A comprehensive laboratory evaluation of the composition of asphalt mixtures containing RAP and/or RAS, with and without rejuvenating agents was conducted. Laboratory testing evaluated molecular composition using SARA, GPC, and intermediate temperature fracture resistance of laboratory produced mixtures using the SCB test. Deconvoluted GPC data allows the identification of associated asphaltene fractions in the aged asphalt binder extracted from RAP, RAS-M and RAS-P. The molecular fractionation through GPC of RAS samples confirmed the presence of associated asphaltenes in great concentrations.

The concentration of RAS asphaltenes exceeds 40 wt. % of which 25 wt. % are highly aggregated with apparent molecular weights approaching 100K. High concentrations of HMW asphaltenes decrease the fracture resistance of the asphalt mixtures. Mixtures with a high content of asphalt cement species with MW > 20K Daltons (asphaltenes) are relatively brittle. Poor intermediate temperature performance was predicted by  $J_c$  values of less than 0.5 kJ/m<sup>2</sup>. Both RAS-M and RAS-P are much more highly oxidized than RAP as indicated by FTIR spectroscopy.

High molecular weight associated asphaltenes are not significantly dissociated by adding rejuvenators. Use of rejuvenators negatively impacted intermediate temperature performance for the mixtures evaluated in this study.

The extent of asphalt extraction from RAS increased with the addition of rejuvenators and generally adversely affected the mixtures fracture resistance at intermediate temperature. This may be explained by the additional RAS binder dispersed in the mixture

The asphaltene component from the SARA analysis was considerably smaller than the asphaltenes determined from deconvoluted GPC chromatograms. The SARA asphaltenes analysis by precipitation did not capture the total amount of associated asphaltenes in the binder as measured by GPC. Some associated asphaltenes may remain in the resin fraction which is not captured by SARA analysis in the method employed.

AC mixtures containing block copolymeric species with MW > 70K can accommodate 5% RAS and retain satisfactory  $J_c$ 's of at least 0.5 kJ/m<sup>2</sup>. The residual polymers in RAP may promote compatibility of 5% RAS in mixtures containing virgin asphalt binder and 15% RAP.



## ACRONYMS, ABBREVIATIONS & SYMBOLS

Å	Angstrom
AASHTO	American Association of State Highway and Transportation Officials
AC	Asphalt Cement
BBR	Bending Beam Rheometer
BHT	Butylated Hydroxyl Toluene
CRM	Crumb Rubber Modifier
DOTD	Louisiana Department of Transportation and Development
DRI	Differential Refractive Index
DSR	Dynamic Shear Rheometer
$\delta$	Delta (Phase Angle)
FHWA	Federal Highway Administration
GPC	Gel Permeation Chromatography
g	Grams
$G^*$	Shear Modulus
HMA	Hot Mix Asphalt
HMW	High Molecular Weight
HPLC	High Performance Liquid Chromatography
$J_c$	Critical Strain Energy
kJ	Kilojoule
LALS	Low Angle Light Scattering
LMS	Large Molecular Size
LTRC	Louisiana Department of Transportation and Development
$\mu$	Micro
M	Million
min.	Minute
mL	Milliliter
MMS	Medium Molecular Size
MMW	Medium Molecular Weight
mv	Millivolt
MW	Molecular Weight
MWD	Molecular Weight Distribution
PAV	Pressure Aging Vessel
PMAC	Polymer Modified Asphalt Cement
QC	Quality Control
RAP	Reclaimed Asphalt Pavement

RI	Refractive Index
RTFO	Rolling Thin-Film Oven
SBS	Poly(Styrene- <i>b</i> -Butadiene- <i>b</i> -Styrene) Triblock Copolymer
SBR	Poly (Styrene-Butadiene) Copolymer
Sec.	Second
SCB	Semi Circular Bend
SEC	Size Exclusion Chromatography
SMS	Small Molecular Size
UV	Ultraviolet
VHMW	Very High Molecular Weight
WMA	Warm Mix Asphalt

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## APPENDIX A

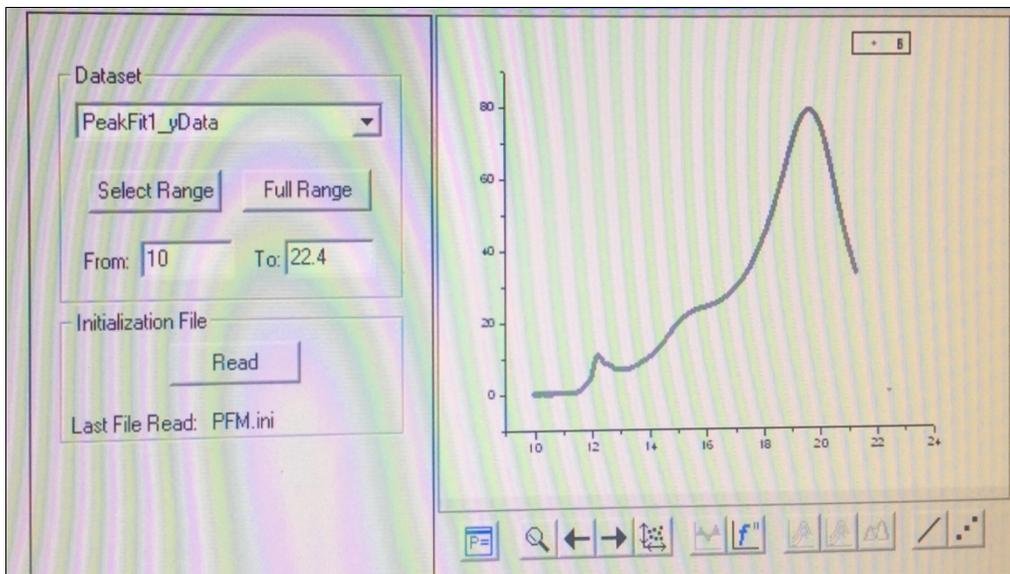
### Quantification of GPC Curves by Integration

As indicated before, the first three eluted fractions are polymers (i.e., very high molecular weight, VHMW, with MW greater than 300,000 Daltons; high molecular weight, HMW, with MW between 45,000 and 300,000 Daltons; and medium molecular weight, MMW, with MW between 19,000 and 45,000 Daltons), followed by asphaltenes (molecular weight from 19,000 down to 3,000 Daltons), and maltenes (molecular weight less than 3000 Daltons) as presented in Figure 10. Quantitative data could be obtained by integration of the area under the curve as shown in Figure 11. For this project, all integrations were performed using the Origin 7 or higher editions [33] as follows.

The base line of the curve should be zero for the whole integration range. The integration Y column (B) is first normalized to 100% by creating a new Y column (column C), the values of which are obtained by dividing the integration column (column B) to the Y/100 number corresponding to that of the last X elution. For example, the 100% integral from Figure 2x was built by dividing the integration column Y (B) to 187/100. The % maltenes are then calculated using normalized data by subtracting from 100 the integral value (read on normalized curve) corresponding to MW 3,000, viz., corresponding to X value (time) for MW 3,000 given by the calibration curve (shown in Figure 9). The % asphaltenes were determined similarly by subtracting from the integral value corresponding to MW 3,000 the number for MW 19,000 given by the calibration curve of Figure 9, and so on for the higher MW fractions (polymers).

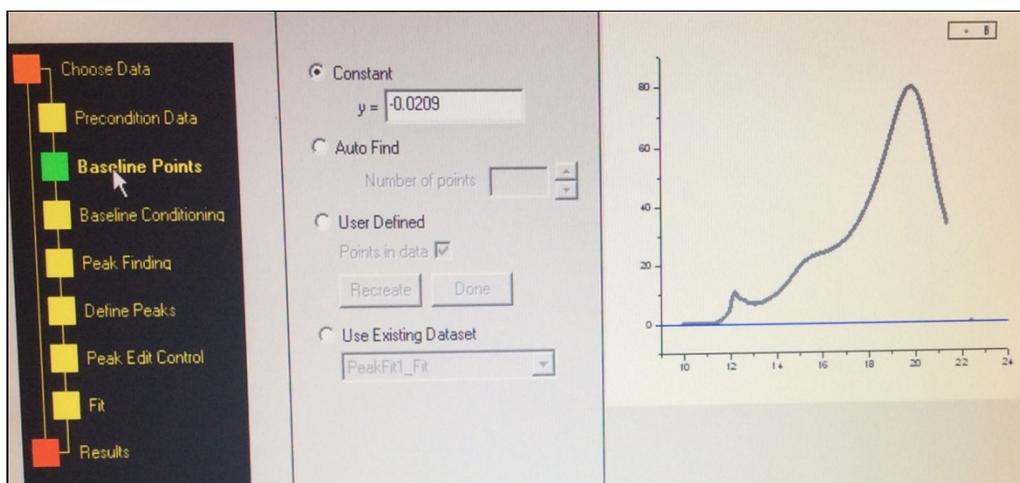
### Deconvolution of GPC Asphalt Species Peaks

The same GPC curve used for integration is considered for deconvolution in peak components. The Origin 7 software is provided with a peak fitting module performing deconvolution of curves in several steps as presented in the following. Considering the GPC trace of the PG 76-22 (containing 5% RAS-P) extracted binder, in the first step the range on X-axis is limited to that of the entire curve (Figure A 1). In the Peak Edit Control step (Figures A 5 and A 6) the peaks defined previously are plotted automatically with a choice of editing the individual peaks until a satisfactory raw fitting is obtained for the original GPC curve.



**Figure A 1**  
**Selecting the range**

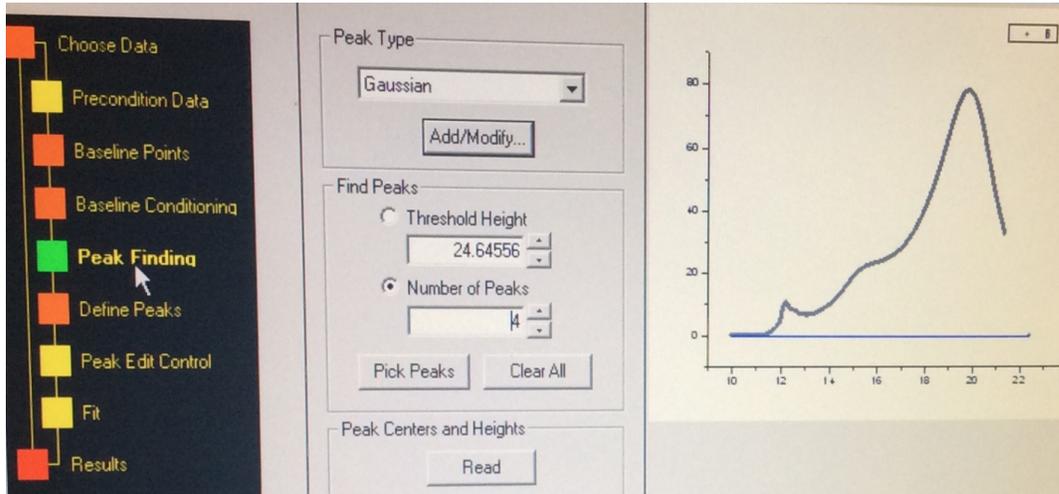
In the next step, the extreme X-axis points are selected (Figure A 2) and the base line is reduced to  $Y=0$ .



**Figure A 2**  
**Selecting the extreme points for the base line**

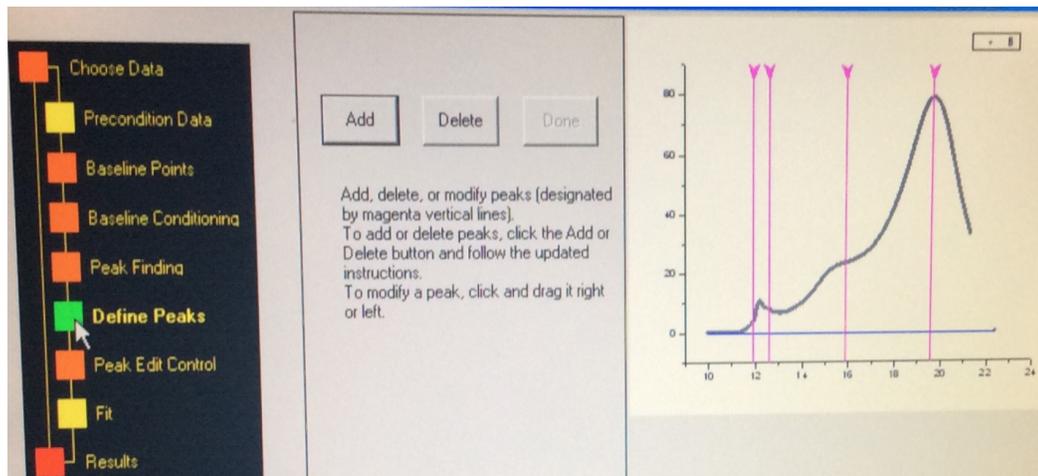
The type (Gaussian) and the number of peaks (4 in this example) are defined as shown in Figure A 3, which is followed by definition of X-axis values corresponding to peak maxima

(Figure A 4). In this step, the number and place of peaks might be modified by adding/deleting as necessary. Placing the peaks might be made in advance (or in parallel in another window) by inspecting the derivative of the GPC curve and selecting the abscissa for peak maxima or peak overlapping maxima ( $X=0$ ).



**Figure A 3**

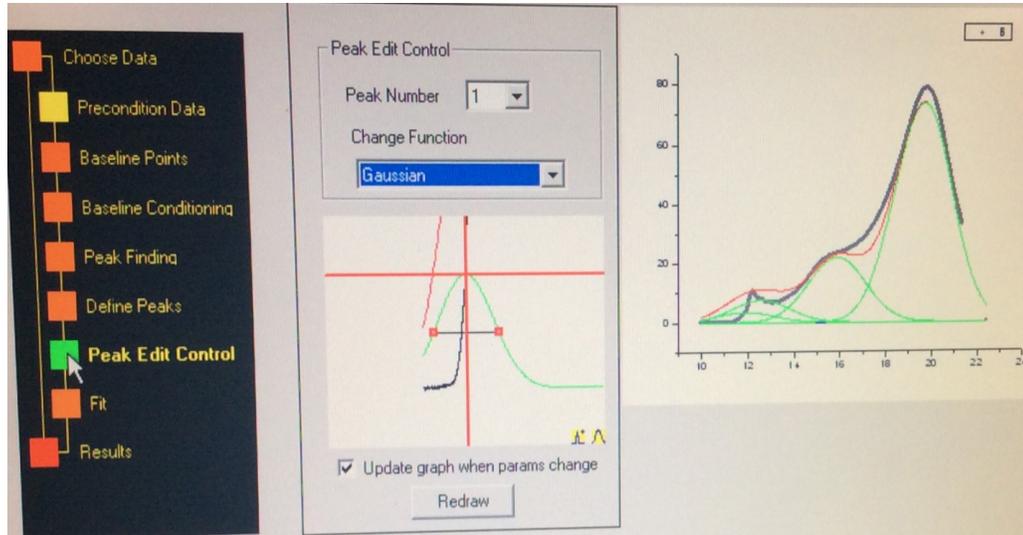
**Selecting the type (Gaussian) and the number of peaks (4 in this example)**



**Figure A 4**

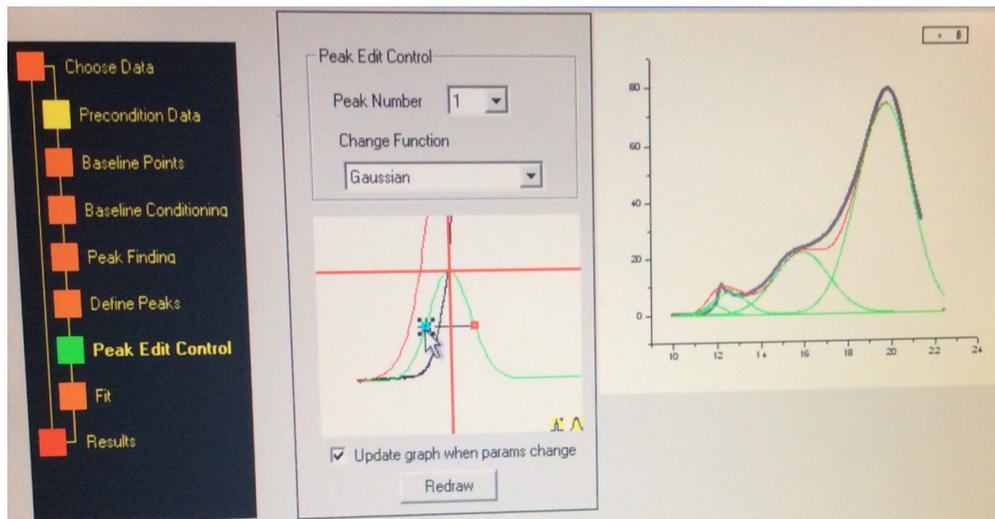
**Peak definition by adding/deleting as necessary**

In the Peak Edit Control step (Figures A 5 and A 6), the peaks defined previously are plotted automatically with a choice of editing the individual peaks (Figure A 5) until a satisfactory raw fitting is obtained for the original GPC curve (Figure A 6).



**Figure A 5**

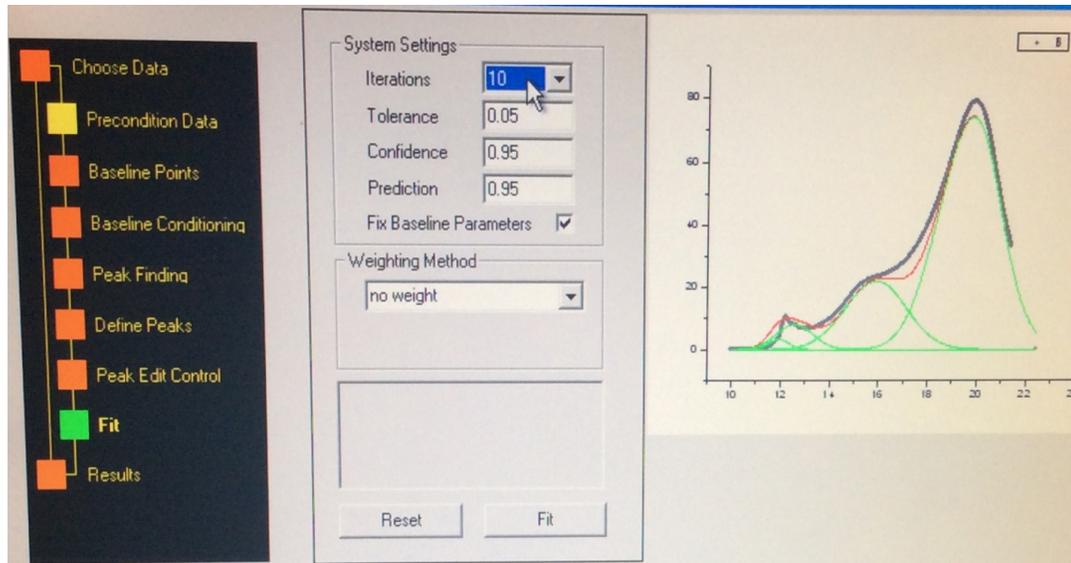
**Editing peak Number 1 after an automated plot of the raw peaks defined in previous step**



**Figure A 6**

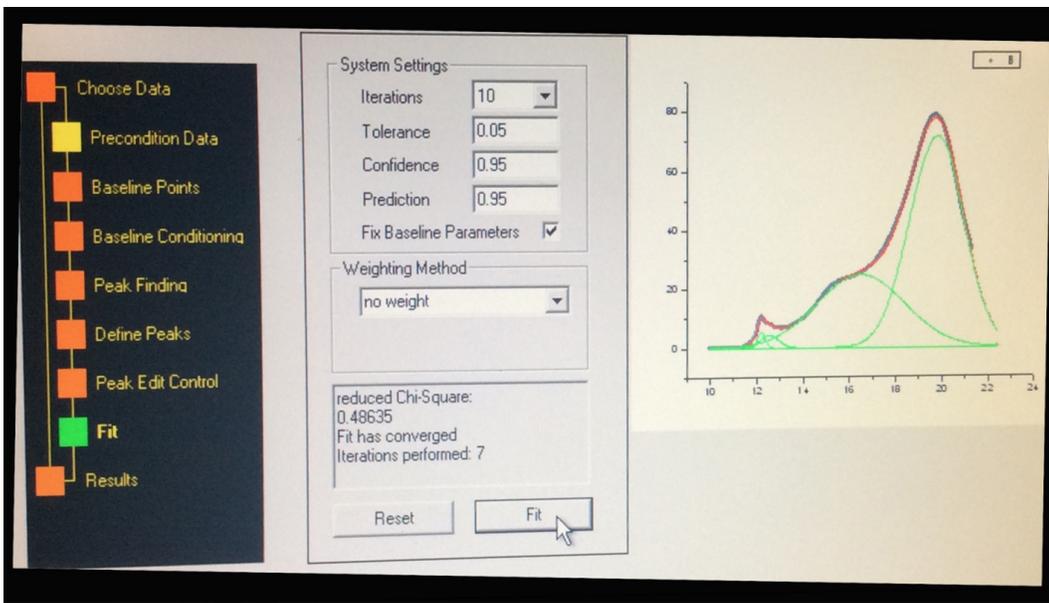
**Redrawing the peaks after editing peak Number 1 in Figure A 5**

Fitting of peaks after the edit and control step is performed by selecting the number of iterations (Figure A 7) for which a satisfactory overlapping of the fitting curve with the original GPC trace is obtained (Figure A 8). The fitting performance does not increase with the number of iterations. According to our experience in fitting the curves, 10 or 100 iterations will give the same result, the quality of the overlapping being dictated by the selection of the peak numbers and by the editing of individual peaks.



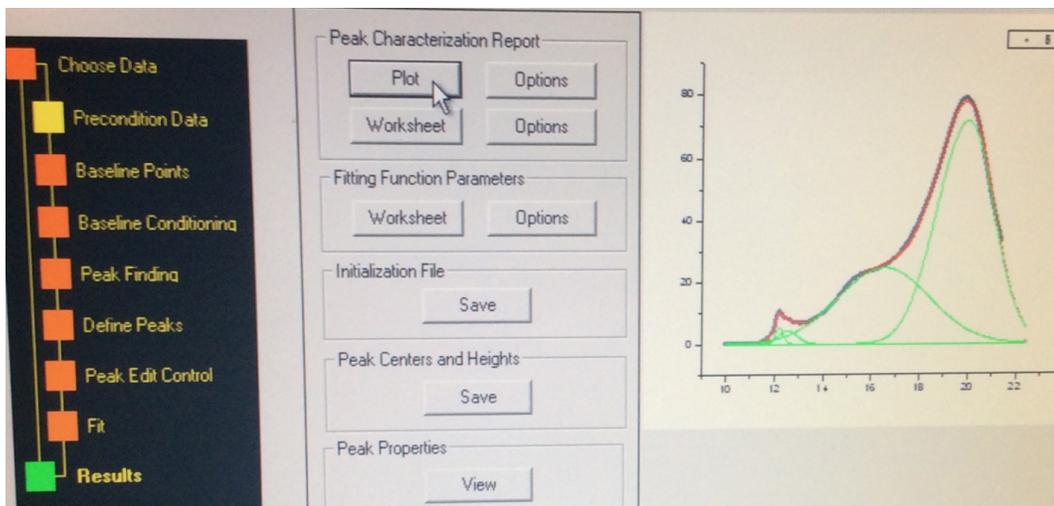
**Figure A 7**

**Definition of system settings (in particular the number of iterations, 10 in this example) for the fitting operation.**



**Figure A 8**  
**The Fit and the resulted peak deconvolution diagram**

The Origin technique gives several choices for the peak characterization report, out of which plotting is preferred (Figure A 9).

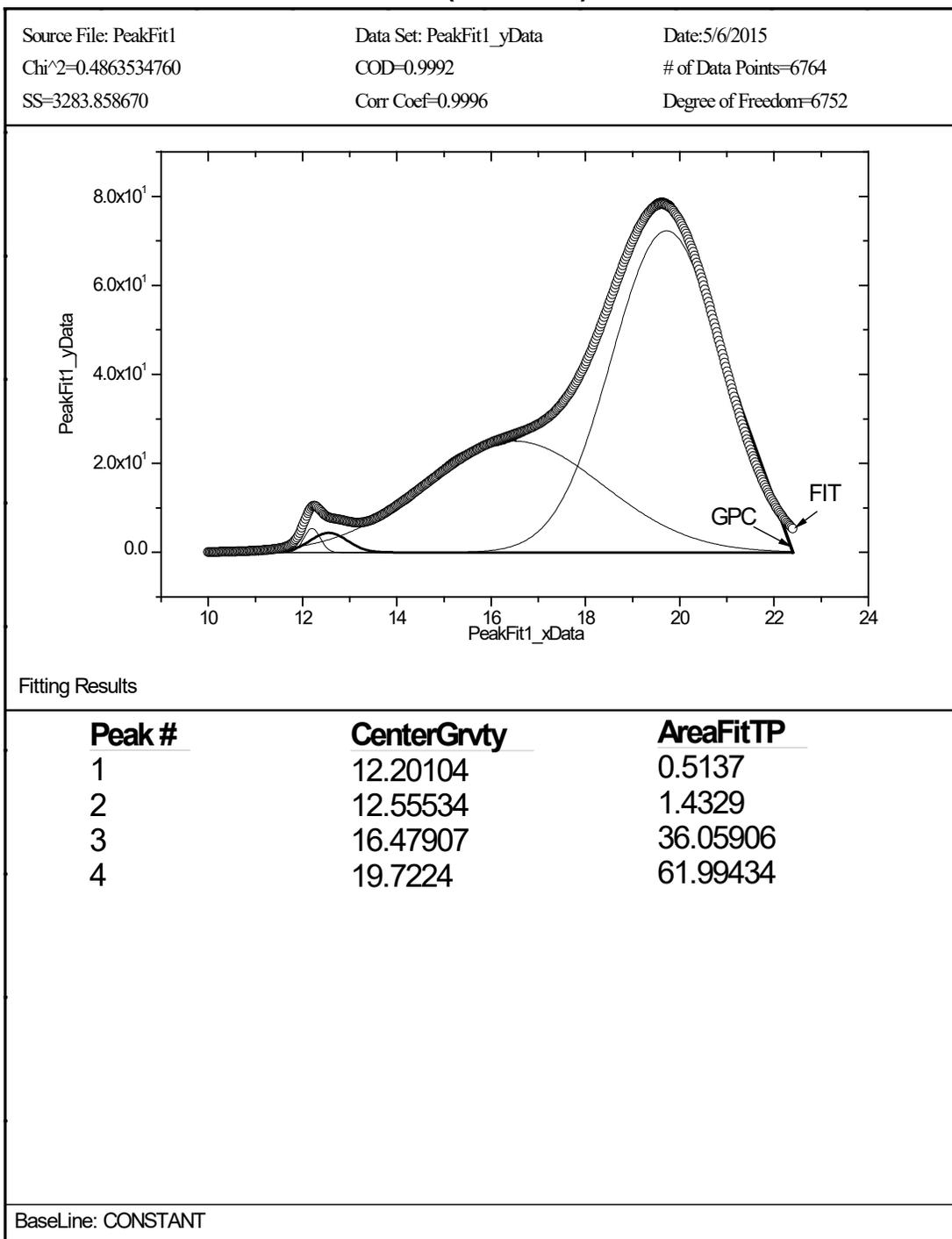


**Figure A 9**  
**Selection of results for report: “Plot” command in this example**

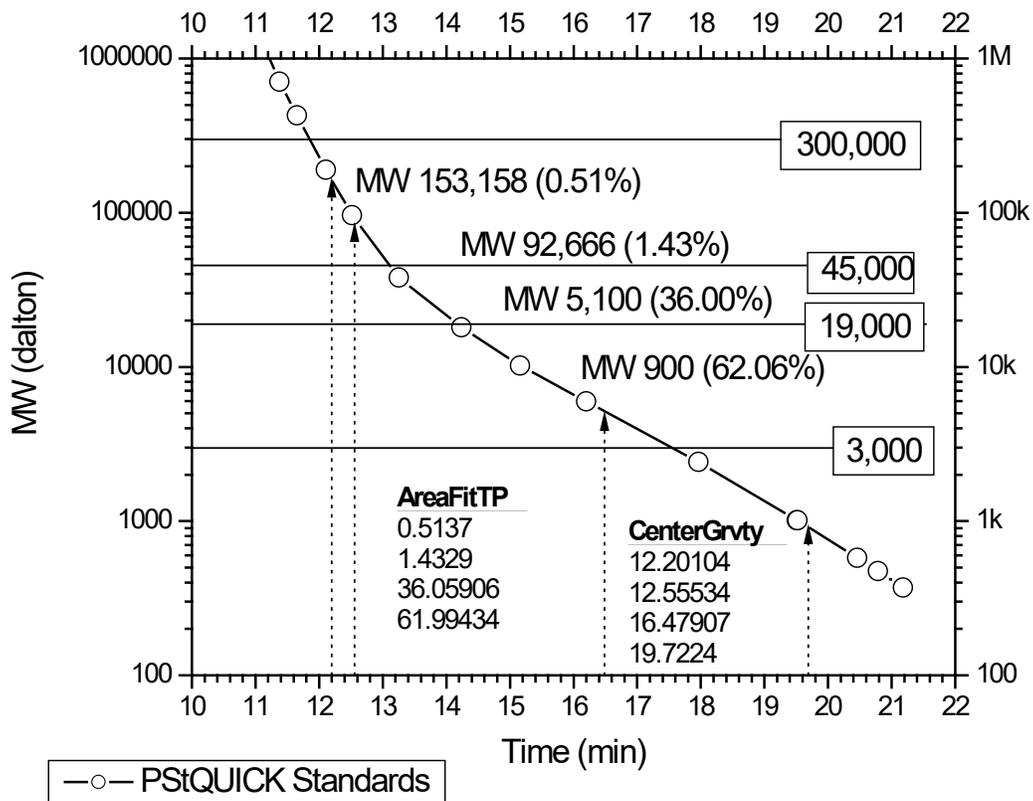
The plot from the report gives information on peak maxima (center of gravity) and on percent contribution of individual peaks (% area fit) to total area covered by the GPC traces

(Figure A 10). These two parameters are used for individual peaks to define the magnitude of MW by reading it on the calibration curve as presented in Figure A 11. Interestingly, the POLYMER peak MW = 100,000 (2%) of Figure 11 is an overlapping of two peaks: one of SBR with MW = 153,158 Daltons (0.51%) and the other corresponding to asphaltenes associations of large molecular weight, i.e., MW = 92,666 Daltons (1.43%)

### PG 76-22 (5% RAS P)



**Figure A 10**  
**Report plot data for defining the place of peaks and their corresponding MW**



**Figure A 11**  
**Determination of MW of peaks according to report plot data**



## APPENDIX B

In order to assure the presence of an acceptable level of polymer in PMAC samples, a GPC analysis is recorded on each sample used in Louisiana construction projects. Careful analysis of the resultant chromatograms allows an estimation of the asphaltene and maltene contents of these samples. The authors reevaluated each chromatogram in the DOTD files and compiled the following data.

### PG-70 Asphalt binders

**Table B 1**

#### Company A PG-70

GPC ID <b>PG-70</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
41UA	0.11	0.85	0.73	1.68	16.33	81.98
752969	0	0.46	0.60	1.05	15.74	83.20
753354	0.06	0.49	0.70	1.25	16.07	82.68
753507	0	0.35	0.63	0.98	15.32	83.70
753911	0.35	0.99	0.83	2.18	15.33	82.49
Mean				1.428	15.758	82.81
Standard deviation				0.501	0.447	0.662

**Table B 2**  
**Company B PG 70**

GPC ID <b>PG 70</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
752973	0	0.46	0.60	1.05	15.74	83.20
752079	0.04	0.96	0.55	1.55	15.63	82.82
753156	0	0.10	0.18	0.29	15.63	84.08
753280	0	0.96	0.52	1.48	15.97	82.54
753353	0.02	0.94	0.43	1.39	15.19	83.42
753377	0.15	1.26	0.94	2.34	13.97	83.69
753378	0	0.33	0.65	0.98	13.30	85.72
753379	0.06	0.76	1.04	1.86	14.26	83.87
753170	0.1	1.18	1.49	2.77	16.03	82.20
750831	0.06	1.11	0.33	1.49	16.10	82.41
753579	0.01	0.87	0.49	1.37	15.14	83.49
753580	0	0.68	0.75	1.44	15.85	82.71
749420	0	0.72	0.17	0.89	14.63	84.48
750147	0.09	1.32	1.18	2.58	17.28	80.14
749723	0	1.02	0.39	1.41	16.61	81.98
753997	0	0.96	0.76	1.72	16.43	81.85
753999	0	1.39	0.49	1.87	13.21	84.92
754000	0.07	1.60	0.69	2.36	13.75	83.89
754110	0.13	1.29	0.67	2.08	15.89	82.03
754149	0.07	1.23	0.47	1.77	15.19	83.04
745501	0	0.74	1.42	2.16	16.51	81.33
754307	0	0.79	0.57	1.36	14.99	83.65
754308	0.26	1.64	0.29	2.19	12.76	85.05

755201	0.11	0.93	0.64	1.68	15.57	82.75
755261	0	0.22	0.32	0.54	16.17	83.29
755265	0.04	1.49	0.70	2.23	14.63	83.14
755396	0	1.0	0.6	1.6	13.84	84.56
755264	0.04	1.12	0.87	2.03	15.39	82.58
755457	0	1.01	0.79	1.8	14.71	83.43
755458	0	0.36	0.29	0.65	13.03	86.32
Mean				1.65	15.11	83.29
Standard deviation				0.60	1.17	1.30

**Table B 3**  
**Company C PG 70**

GPC ID <b>PG 70</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K-19K %			
753754	0	0.93	0.83	1.76	13.70	84.54
749459	0.02	1.16	0.57	1.74	13.28	84.98
753996	0	1.19	0.62	1.81	13.23	84.96
749457	0	0.99	0.22	1.21	12.68	86.11
753885	0	0.88	0.83	1.71	13.73	84.56
753878	0	1.15	0.41	1.56	12.56	85.88
755275	0	1.06	0.86	1.92	13.2	84.88
755274	0	0.92	0.76	1.68	12.42	85.90
Mean				1.67	13.10	85.23
Standard deviation				0.21	0.50	0.64

**Table B 4**  
**Company D PG 70**

GPC ID <b>PG 70</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
753153	0.09	1.03	0.68	1.81	18.0	80.2
749489	0	0.82	0.46	1.28	16.79	81.93
753172	0	0.96	0.55	1.51	17.97	80.52
753811	0.06	1.19	0.40	1.65	16.80	81.55
755696	0.07	1.15	0.60	1.88	16.23	81.89
755697	0.01	1.24	0.68	1.93	16.45	81.62
Mean				1.68	17.04	81.29
Standard deviation				0.25	0.76	0.74

**Table B 5**  
**Company E PG -70**

GPC ID <b>Martin Asphalt PG -70</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
753471	0.29	3.91	0.57	4.76	12.35	82.89
753463	0	1.12	0.34	1.45	11.83	86.72
754312	0.03	1.39	0.11	1.53	11.91	86.56
754314	0.3	1.67	0.5	2.48	13.25	84.27
Mean				2.56	12.34	85.11
Standard deviation				1.54	0.65	1.86

**Table B 6**  
**Company F PG-70**

GPC ID <b>Pelicon</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K-300K %	300K-45K %	45K-19K %			
22747195	0.05	0.85	0.67	1.56	17.12	81.32

**Table B 7**  
**Company G PG-70**

GPC ID <b>Huntsouth land PG-70</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K-300K %	300K-45K %	45K-19K %			
755454	0	0.72	1.24	1.96	18.62	79.42
755455	0	0.69	1.22	1.91	18.69	79.40
Mean				1.94	18.66	79.41
Standard deviation				0.04	0.05	0.01

**PG -76 Asphalt Binders**

**Table B 8  
Company A PG-76**

GPC ID <b>PG-76</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
41AT	0.59	1.87	0.6	3.06	15.23	81.71
746307	0	1.5	1.06	2.56	17.13	80.31
753115	0.07	2.41	0.91	3.39	15.64	80.97
751618	0.44	1.37	0.57	2.38	14.81	82.81
753177	0.04	2.4	0.94	3.38	16.25	80.37
750765	0.09	2.6	0.89	3.58	15.88	80.54
755270	0.08	2.18	1.39	3.65	15.25	81.10
755262	0.50	2.48	0.74	3.72	12.65	83.63
755263	0.18	1.7	0.72	2.6	12.97	84.43
755266	0.36	1.83	0.68	2.87	12.89	84.24
755400	0.08	1.74	1.41	3.23	15.92	80.85
755553	0	2.06	1.12	3.18	14.65	82.17
Mean				<b>3.13</b>	<b>14.94</b>	<b>81.93</b>
Standard deviation				<b>0.45</b>	<b>1.43</b>	<b>1.51</b>

**Table B 9**  
**Company B PG-76**

GPC ID <b>PG-76</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
751028	0.17	1.27	0.49	1.92	15.5	82.58
751334	0.17	2.56	0.74	3.47	16.08	80.45
753111	0.03	2.01	1	3.04	15.93	81.03
751028	0.24	1.36	0.66	2.26	15.42	82.32
753178	0	2.27	0.5	2.77	14.36	82.87
753167	0.03	1.26	1.18	2.48	15.48	82.05
753472	0.17	2.86	1.08	4.11	15.7	80.19
753523	0	2.38	0.85	3.23	15.45	81.32
751471	0	1.59	0.13	1.72	13.31	84.97
751478	0.09	2.25	1	3.34	15.65	81.01
753176	0	2.35	0.83	3.18	14.98	81.84
750839	0	2.29	0.51	2.80	14.78	82.42
750843	0.27	2.91	0.87	4.05	15.9	80.05
750833	0.02	2.36	0.76	3.14	15.28	81.58
750835	0.06	2.66	0.68	3.4	15.58	81.02
750846	0.10	2.67	0.5	3.27	14.62	82.11
757475	0	2.18	0.93	3.11	15.22	81.67
753599	0.14	2.2	1.27	3.61	15.45	80.94
753603	0	1.96	1.37	3.33	15.79	80.88
751470	0	2.41	0.8	3.21	15.11	81.68
753597	0.01	2.2	1.32	3.53	16.44	80.03
753601	0	1.76	1.2	2.96	15.69	81.35
750844	0.22	2.78	0.6	3.60	14.94	81.46

GPC ID <b>PG-76</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K- 300K %	300K- 45K %	45K- 19K %			
750845	0.09	2.47	0.92	3.48	15.68	80.84
751473	0.04	2.38	1.04	3.46	15.78	80.76
753620	0	2.01	1.3	3.31	12.69	84.00
753738	0	1.77	1.19	2.96	15.41	81.63
753734	0.03	2.08	1.19	3.30	15.78	80.92
753786	0.05	1.74	0.81	2.6	12.93	84.47
751476	0.03	0.71	0.67	1.41	15.22	83.37
753619	0	2.37	0.92	3.29	15.1	81.61
749415	0	2.76	0.57	3.33	14.82	81.85
749418	0.06	2.54	0.61	3.21	15.02	81.77
753806	0.15	2.09	1.29	3.53	15.84	80.63
750833	0.2	2.47	1.06	3.73	16.02	80.25
753599	0.11	2.16	1.36	3.63	15.77	80.6
753603	0	1.91	1.33	3.24	15.48	81.28
750843	0.18	2.55	0.61	3.34	15.4	81.26
753879	0.11	1.99	1.1	3.2	12.88	83.92
751473	0	2.08	0.91	2.99	15.21	81.8
751475	0.09	2.3	1.01	3.4	15.52	81.08
750835	0.33	2.92	0.88	4.13	15.91	79.96
750845	0	2.19	0.86	3.05	16.17	80.78
751470	0.03	2.45	0.88	3.36	15.78	80.86
750839	0.02	2.46	0.91	3.39	16.86	79.75
750842	0.17	2.59	0.72	3.48	16.25	80.27
750844	0.1	2.54	0.58	3.22	15.86	80.92
750846	0.18	2.8	0.88	3.86	17.34	78.8

GPC ID <b>PG-76</b>	Polymer molecular weights & %			Total Polymer % <b>1000K – 19K</b>	Asphaltene% <b>19K-3K</b>	Maltene % <b>&lt; 3K</b>
	1000K-300K %	300K-45K %	45K-19K %			
749419	0.15	2.41	0.83	3.39	15.98	80.63
748274	0.23	2.34	0.78	3.35	17.13	79.52
753883	0	1.62	1.09	2.71	12.31	84.98
754112	0.11	2.19	1.16	3.46	17.51	79.03
754204	0.41	2.29	1.1	3.8	15.72	80.48
745740	0.21	2.56	0.94	3.71	15.95	80.34
754250	0.23	2.44	0.8	3.47	17.07	79.46
754306	0	1.32	0.92	2.24	15.57	82.19
755197	0	2.34	0.46	2.8	15.53	81.67
755267	0	2.22	0.86	3.08	14.62	82.3
755268	0.04	1.91	1.31	3.26	15.55	81.19
755276	0.46	1.75	0.75	2.96	14.41	82.63
755398	0	1.76	1.3	3.06	14.84	82.1
755456	0	1.92	1.05	2.97	16.51	80.52
755405	0	1.77	1.16	2.93	14.74	82.33
Mean				3.18	15.41	81.41
Standard deviation				0.51	1.01	1.30



## APPENDIX C

### Analysis of Polycyclic Aromatic Compounds (PAHs) in Virgin Asphalt and its Mixture with RAP and RAS

#### Background

The United States Environmental Protection Agency (EPA) has shown concern about the emission of volatile organic compounds and PAHs, which are formed when products like coal oil, gas, garbage, and sometimes old asphalts are burned [44]. PAHs are a group of over 100 different chemicals consisting of carbon and hydrogen in a fused ring structure. The EPA has compiled a list of 16 compounds, (shown in Figure 1) which are considered harmful, toxic, and persistent in the environment. The PAHs present in the fumes released from asphalts binders during road paving (especially in hot-mix asphalts), can be hazardous to human health. It can also enter the water supply when it mixes with rain. The amounts of PAHs in asphalt or recycled asphalt, depends on the chemical complexity of the source from which the asphalt is derived from. Virgin asphalt generally has a low concentration of PAHs. This is because during vacuum distillation, most of the low molecular mass compounds with low boiling points including 3 to 7 aromatic fused rings will be removed. As a result, these asphalts contain small amounts of these compounds. Recycled asphalts may have more PAHs because of the inclusion of compounds added for the desired performance (e.g., flux, coal tar, solvents, aromatics etc.) or if they were in contact with coal tar. Coal tar contains a very high concentration of PAH compared to virgin asphalt. Hence the use of recycled asphalts, especially asphalts from parking lots and roofing, should be tested for PAH. Studies show that the presence of the PAH compounds may increase the risk of cancer [56, 57].

The use of recycled asphalt pavement (RAP) and shingles (RAS) in virgin asphalt binder is an increasing trend in road construction due to its economic and environmental benefits. In project 12-3B, the authors incorporated different percentages of RAP and RAS along with virgin asphalt. The researchers analyzed the recycled binders for the presence of polycyclic aromatic hydrocarbons (PAH). It is anticipated that recycled asphalt pavements (RAP) and recycled asphalt shingles (RAS) may contain PAHs. Recycling these products without testing their PAH content can increase the presence of these harmful compounds in nature through atmospheric emission and HMA production. In project 12-3B, the PAH content of the asphalt mixtures were determined. This ensured that the correct material was used, reducing or even avoiding environmental and human contamination. In this project, the researchers tested RAP, RAS, PG 64-22 and a blend of PG 64-22 &RAP using a reported procedure which consists of an extraction followed by Gas Chromatography/Mass Spectroscopy (GC/MS) analysis.

## Methodology

### **Removal of Asphaltenes from Asphalt using Precipitation [58]**

For the PAH analysis, the first step was to remove the high molecular weight asphaltenes from the asphalt samples, to minimize extraction and analytical complications. This was done by precipitating the asphaltenes from the asphalt binder using dichloromethane (DCM) and hexane. Asphalt samples (0.5 g) were weighed into a 10 mL beaker and dissolved in 5 mL of DCM. After complete dissolution, it was transferred carefully into a 100 mL standard flask using another 5 mL of DCM. The standard flask was filled with n-hexane to the mark. It was sonicated for 5 minutes and the samples were allowed to settle overnight. The solution was filtered and 20 mL of the filtrate (maltenes fraction) was used for further extraction.

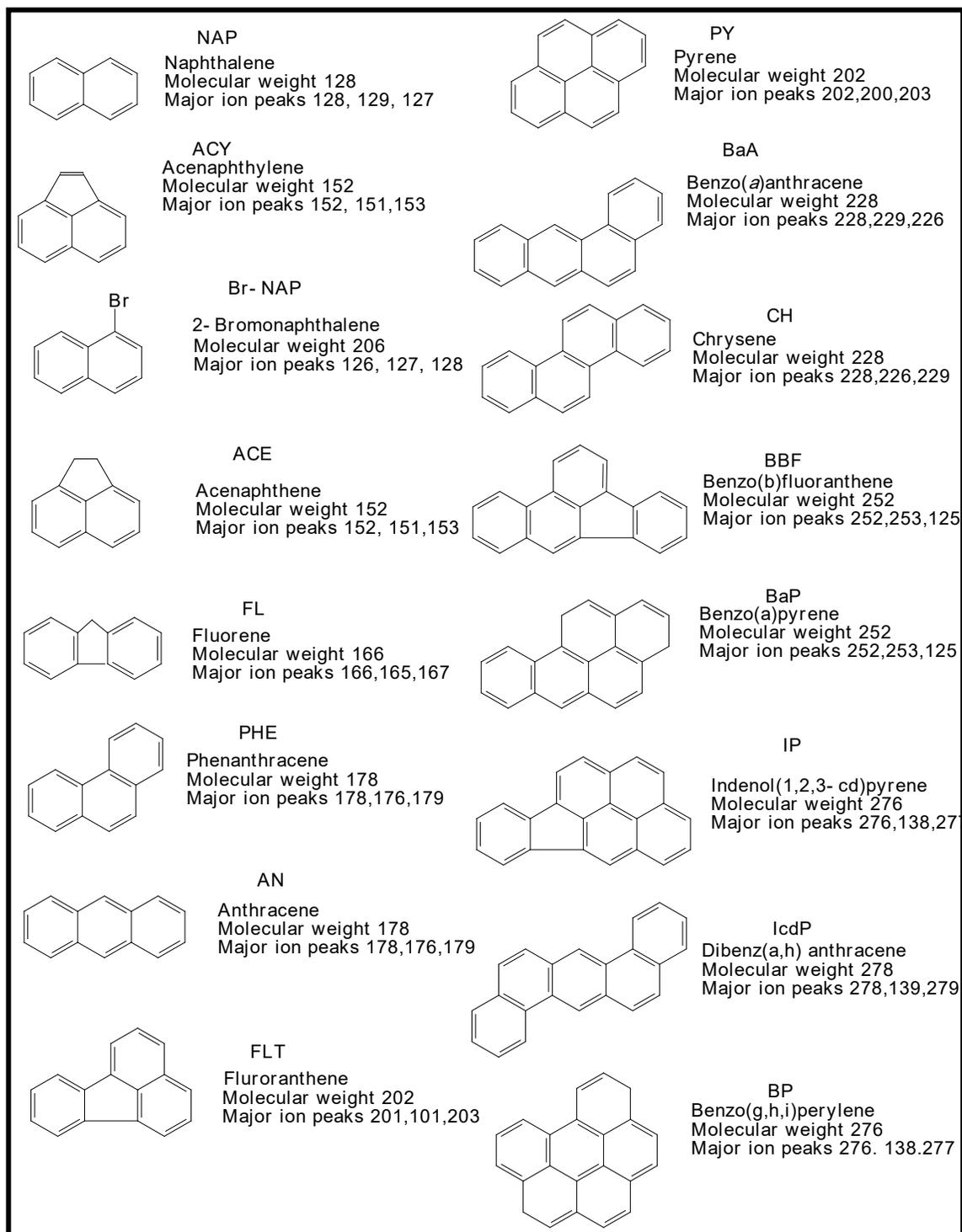
### **Extraction of PAH Compounds from the Maltene Fraction of the Asphalt [60]**

Twenty mL of the maltenes fraction was concentrated to 5 mL. This was extracted three times with DMSO (2.5 mL $\times$  3). That removed the aliphatic compounds. To the DMSO solution, 10 mL of water was added and extracted thrice (5 mL, 2 mL and 2 mL) with iso-octane. The iso-octane layer was extracted thrice with DMSO (2.5 mL $\times$  3). To the DMSO solution, 10 mL of water was added and this solution was back extracted thrice into iso-octane. The iso-octane layer was then passed through a small plug of anhydrous sodium sulfate to remove any water present in it. It was then dried and the sample obtained, was dissolved in 1 mL of DCM and used for GC/MS analysis. The internal standard used was 2-fluoro-biphenyl.

### **GC/MS Analysis**

PAH analysis was done using a Varian Saturn GC connected to a Varian Saturn ion trap mass detector. Separation was carried out in an Agilent DB-5 column (30 $\times$ 0.25mm i.d, 0.25- $\mu$ m film thickness) using the split less mode (0.75 min. purged). In the beginning, the column oven temperature was kept at 60 $^{\circ}$ C for 10 minutes, and then increased to 120 $^{\circ}$ C at rate of 5 $^{\circ}$ C/minute and then to 300 $^{\circ}$ C at a rate of 3 $^{\circ}$ C/minute. The temperature of injector was 280 $^{\circ}$ C and the temperature of the detector was 300 $^{\circ}$ C. The sample volume was 1 $\mu$ L and the carrier gas was helium (1mL/minute). Calibration (using PAH standards): 16- component PAH standard was obtained and had a concentration of 2000  $\mu$ g/mL in DCM. The stock was diluted to get four different concentrations of 0.512, 3.84, 6.4, and 12.8  $\mu$ g/mL. All solutions were prepared in DCM.

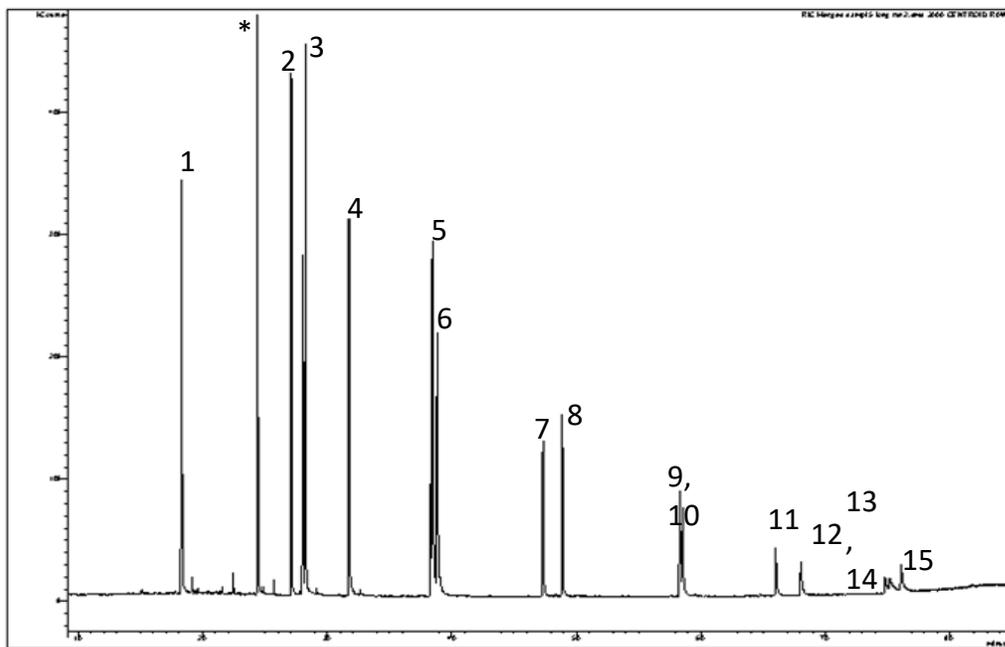
Calibration of the GC/MS was effected with a standard PAH mixture (Figure C 1).



**Figure C 1**  
Chemical structure and molecular weight of the 16 PAHs present in a standard mix.

## Discussion of Results

A multipoint calibration with four standard solutions (16-component PAH mixture) was used for the linearity verification. Figure C 2 shows the typical separation obtained for the PAH mixture by the GC column in this study.



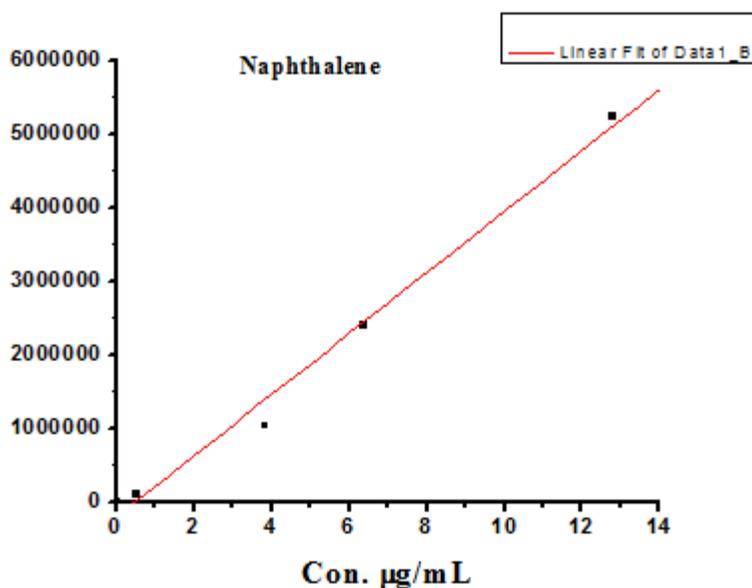
**Figure C 2**

**Chromatogram of a 1 $\mu$ L injection of 6.4 $\mu$ g/mL standard solution (the name of the compound corresponding to the numbers are given in Table 1 ) \* internal standard**

**Table C 1**  
**Polycyclic compounds in standard PAH mixture**

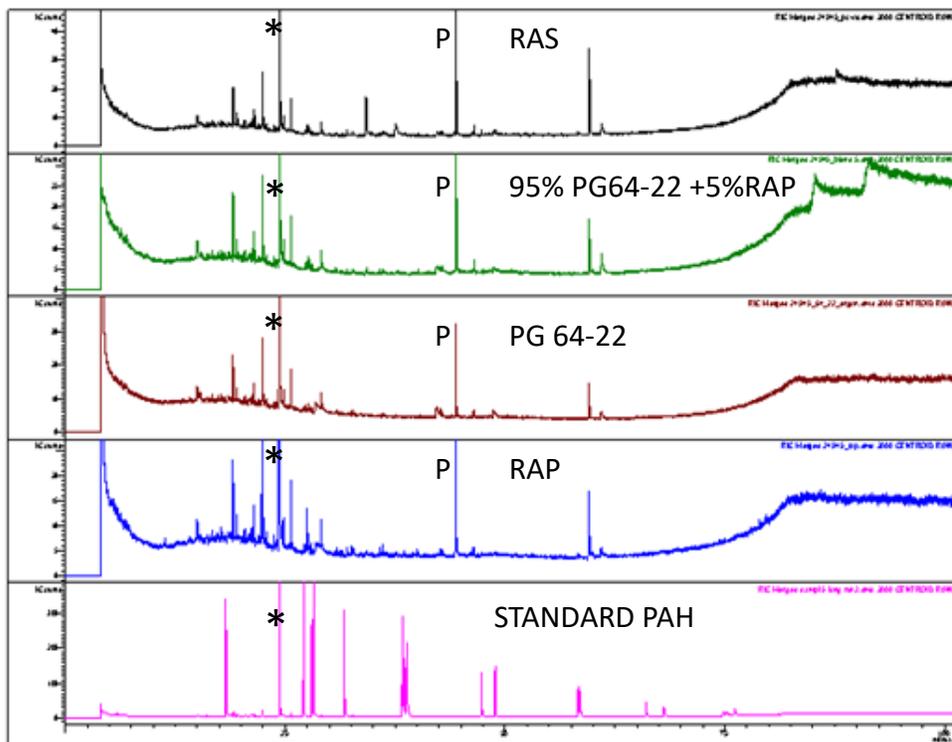
No.	Name of the compound eluted	No.	Name of the compound eluted
1	Naphthalene	9	Benzo[ <i>A</i> ]Anthracene
2	Acenaphthylene,	10	Chrysene
3	Acenaphthene	11	Benzo[ <i>B</i> ]Fluoranthene
4	Fluorene	12	Benzo[ <i>A</i> ]Pyrene
5	Phenanthracene	13	Indenol[1,2,3- <i>Cd</i> ]Pyrene
6	Anthracene,	14	Dibenz[ <i>A,H</i> ]Anthracene
7	Fluoranthene	15	Benzo[ <i>Ghi</i> ]Perylene
8	Pyrene	*	Internal standard

Linearity was present across the ranges of concentration studied, giving a coefficient of variation between 0.980-0.995. An example linear regression plot obtained for naphthalene is shown in Figure C 3.



**Figure C 3**  
**Example of linear regression plot –calibration curve of naphthalene**

The researchers selected 4 asphalt binders for the extraction and PAH analysis: PG 64-22 virgin binder, RAP, RAS & a blend of 5% RAP in PG 64-22. The maltene fraction of the samples was used for the analysis to avoid complication in the extraction procedure. An extraction method using DMSO solvent was selected. A maltene solution in hexane was extracted with DMSO, which was then back extracted into iso-octane. The procedure was repeated twice to get the samples. The detection limit of this method is 1.0 ppm. After extraction, 1 $\mu$ L of the concentrated solution was injected in to GC to separate the components present in the sample. The separated peaks were analyzed based on the chromatogram of the standard mixture sample. Chromatograms obtained for the 4 asphalt samples are shown in Figure C 4, along with the standard solution containing 16 PAHs. There was no detectable level of PAH in any of the four tested samples. If at all present, it should be in the trace levels which the method adopted could not determine. Earlier studies in asphalt and RAP samples also showed similar results of its presence in below detection limit<sup>4</sup>.



**Figure C 4**

**Chromatograms of asphalt samples and standard PAH mix. \* Represents the internal standard, P represents the phthalate impurity in asphalt samples.**

**Table C 2**  
**Analytical results from asphalt samples**

Polyaromatic hydrocarbons	PG 64-22	RAS	RAP	PG 64-22 (90%)+ RAP (5%)+RAS (5%)
Naphthalene	BDL	BDL	BDL	BDL
Acenaphthylene	BDL	BDL	BDL	BDL
Acenaphthene	BDL	BDL	BDL	BDL
Fluorene	BDL	BDL	BDL	BDL
Phenanthracene	BDL	BDL	BDL	BDL
Anthracene	BDL	BDL	BDL	BDL
Fluoranthene	BDL	BDL	BDL	BDL
Pyrene	BDL	BDL	BDL	BDL
Benzo[ <i>A</i> ]Anthracene	BDL	BDL	BDL	BDL
Chrysene	BDL	BDL	BDL	BDL
Benzo[ <i>B</i> ]Fluoranthene	BDL	BDL	BDL	BDL
Benzo[ <i>A</i> ]Pyrene	BDL	BDL	BDL	BDL
Indenol[1,2,3- <i>Cd</i> ]Pyrene	BDL	BDL	BDL	BDL
Dibenz[ <i>A,H</i> ]Anthracene	BDL	BDL	BDL	BDL
Benzo[ <i>Ghi</i> ]Perylene	BDL	BDL	BDL	BDL

BDL =below detection limit

### **Conclusion**

Analysis of asphalt samples, (PG 64-22, RAP, RAS) showed that the compounds do not contain (or contain in below the level detection), polycyclic aromatic hydrocarbons(PAH). So the recycled materials used in this study are safe to use.

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