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16. Abstract

This research demonstrated the application of gel permeation chromatography (GPC) as an analytical tool to ascertain the amounts of polymer modifiers in polymer modified asphalt cements, which are soluble in eluting GPC solvents. The technique was applied to 29 samples from five refineries supplying asphalt mixes to Louisiana. Addition of recycled asphalt pavement (RAP) during the mixing process increases the asphaltene content with a corresponding decrease in the maltenes content. An assessment of the extent of oxidative aging of modified asphalt binders during the paving process confirmed minimal changes during the paving process. Field aging of mixes containing RAP is slower than that predicted by rolling thin film oven (RTFO) laboratory aging, suggesting that addition of 20 wt% RAP is beneficial.

Although suppliers are using different types of poly(styrene-b-butadiene-b-styrene) (SBS) at different percentages to meet the requirements for a PG 70-22, the authors observed that 1 wt% up to 1.98 wt% polymer is added. To achieve PG 76-22, the authors observed that a minimum of 2 wt% polymer is added. The GPC test method can identify the type of polymer used as well as the percentages of polymer and asphaltenes present.

The content of crystallizable species of selected asphalt binders determined by differential scanning calorimetry (DSC) is presented together with the binder glass transition temperature more accurately determined by dynamic mechanical analysis (DMA).

A method for quantification of GPC solvent insoluble crumb rubber modifier present in crumb rubber modified binders was developed.

The application of the GPC technique to forensic studies of pavement problem issues is demonstrated.

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A Comparative Analysis of Modified Binders:
Original Asphalt and Material Extracted from Existing Pavement

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ABSTRACT

This research demonstrated the application of gel permeation chromatography (GPC) as an analytical tool to ascertain the amounts of polymer modifiers in polymer modified asphalt cements, which are soluble in eluting GPC solvents. The technique was applied to 29 samples from five refineries supplying asphalt mixes to Louisiana. Addition of recycled asphalt pavement (RAP) during the mixing process increases the asphaltene content with a corresponding decrease in the maltenes content. An assessment of the extent of oxidative aging of modified asphalt binders during the paving process confirmed minimal changes during the paving process. Field aging of mixes containing RAP is slower than that predicted by rolling thin film oven (RTFO) laboratory aging, suggesting that addition of 20 wt% RAP is beneficial.

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IMPLEMENTATION STATEMENT

LADOTD has specified, since 1994, the use of polymer modified asphalt cements to improve asphalt pavement performance. However, several critical questions associated with the analysis of polymer modified asphalt cements remain to be solved. 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:

- Developed an effective asphalt binder extraction methodology without affecting the binder properties.
- Developed a simple GPC procedure for determining the composition of asphalt binders based upon the molecular size of the components.
- Evaluated the changes in binder composition during processing and after one year of field aging.
- Demonstrated the positive features of RAP addition to polymer modified asphalt cements (PMACs).
- Illustrated the forensic application of GPC to resolving mix problems encountered in the field.

The findings suggest that the state asphalt laboratory should purchase GPC equipment and integrate GPC analyses into routine PMAC characterizations. Voucher samples of each job including added RAP should be analyzed since these samples reflect the material laid on the road.

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INTRODUCTION

Background and Significance of the Research

During oxidative aging, polar and aromatic molecules interact through attractive forces to form molecular associations resulting in significant changes in the physical properties of asphalts. One consequence is that these associations have effective molecular weights and hydrodynamic volumes larger than the true molecular weights of their components. Therefore, a separation should be possible by techniques that separate mixtures into fractions of different molecular size. The most common technique used to effect this separation is gel permeation chromatography; there are many reports of earlier asphalt separation by this method *[1]*. Gel permeation chromatography is also a fast and reliable method to determine the polymer content in asphalt. Since polymer molecules typically exhibit molecular weights 100 times greater than those of asphalt molecules, they can be easily identified using this method.

A 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. In the case of SBS and styrene-butadiene rubber (SBR) polymer modified asphalt cements (PMACs), there is a large difference (*ca*. two orders of magnitude) between the molecular mass of polymer molecules and the mass of asphalt components. Due to this difference, the polymer can be easily visualized through a size exclusion analysis techniques, such as GPC. As shown previously, the polymer and asphalt components of polymer modified asphalt cements could be separated completely using gel permeation chromatography *[2][3]*. This is shown in Figure 1, which illustrates the GPC traces of PMAC dissolved in tetrahydrofuran (THF) solution and of poly(styrene-b-butadiene-b-styrene) SBS dissolved in decalin solution. The samples are injected onto a set of porous columns and eluted with THF. The order of elution is related to the molecular weight of the component. High molecular weight species elute first followed by molecules with ever decreasing molecular weight. As this figure shows, the SBS polymer elutes at the lowest volume (16-18 mL) and the asphalt begins to elute at volumes greater than 22 mL. Any species eluting at less than 22 mL is of molecular weight higher than that of the largest asphalt species. The polymer eluted at volumes corresponding to polystyrene species of molecular weights of > 530,000 and 90,000 Daltons. The asphalt peak appears at MW = 1.1 K. The decalin is seen as a peak of low intensity at MW = 0.14 K. The differential refractive index, ΔRI, scale was displaced for clarity *[3]*. Changes in the molecular weights of the PMAC components can be followed using GPC. For example, oxidative aging can drastically reduce the molecular weight of polymeric species and change the degree of aggregation of the asphatenes. This is shown in Figure 2 for a polymer modified asphalt binder aged by pressure aging vessel (PAV) treatment

[4]. After one PAV treatment, the peak at 16-17 mL associated with the high molecular weight SBS broadened and spread over elution volumes ranged from 17 to 22 mL. The broadening is due to the cleavage of polymer molecules leading to lower molecular weight molecules that elute at the higher volumes. Also note that the area under the region of the curve from 20 to 23.5 mL increased. This can be attributed to association of asphaltenes leading to higher molecular weight aggregates.

It is of interest to apply GPC methodology to follow the processing and paving sequences and to determine the changes in the mix during its lifetime. The research involves quantitatively assessing: (1) the amount of the polymeric species in a PMAC as received from a supplier, including changes imparted by the addition of RAP to the mix; (2) the amount of the polymeric modifier in the liquid extracted from cores taken from a new road paved with the same PMAC as that received from a supplier; and (3) to assess the extent on the road degradation of the polymeric species by oxidative aging for periods up to 20 months. The research will be extended to evaluate mixes containing a crumb rubber modifier (CRM), which is practically insoluble in GPC solvents. The crumb rubber can be separated and quantified from very dilute solutions (0.1%) of CR modified asphalt binders in which the crumb rubber is present as a loose gel by adding a precipitating solvent/non-solvent mixture.

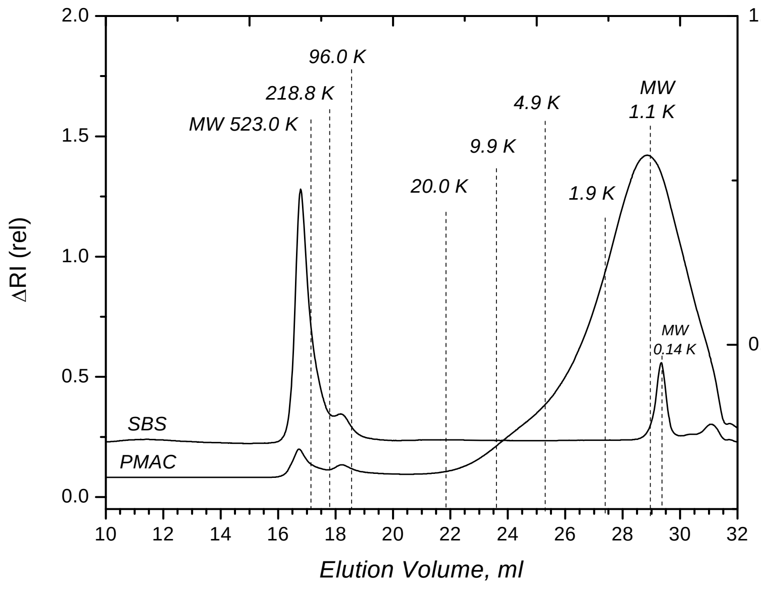

Figure 1
GPC traces of PMAC from THF solution and of SBS from decalin solution (molecular weight of decalin MW = 140 Daltons)

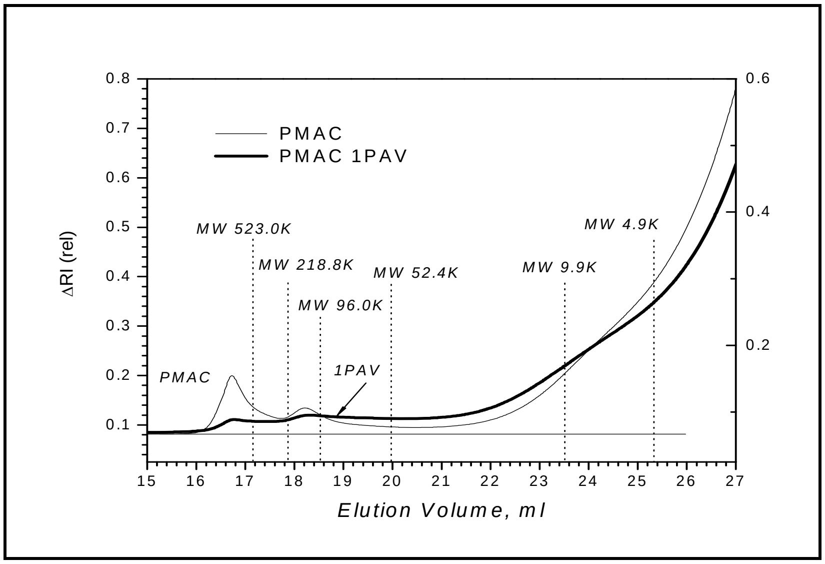

Figure 2
GPC traces of original and PAV aged PMAC samples

Additional Binder Tests

Thermal Analysis

DSC is widely used for determination of thermal transitions brought about by the first order transitions, such as melting and crystallization of crystallizable species. Glass transition, T_g, credited as a second order phenomenon taking place in the amorphous region of the sample, can be also defined by DSC, but it depends largely on the nature of the material and its content of crystallizable fractions. By allowing the temperature to oscillate in a sinusoidal fashion, a clear distinction can be made on the short time scale of the transition between non-reversible phenomena, such as the first order transitions and reversible glass transition *[11, 12]*. The technique, which is very sensitive to thermal transitions, is performed on very small asphalt samples (~10 mg) to ascertain the physical state of the material. Below the glass transition temperature, asphalt behaves like a glass and appears brittle.

Dynamic Mechanical Analysis

The DMA technique characterizes the variation of the dynamic complex modulus (E*) and its components (E', E", and tanδ) with temperature. In this test, a beam sample is subject to a cyclic, torsional strain-controlled loading while the temperature is linearly decreased until failure occurs. The glass transition can be detected using DMA by identifying the temperature at which E" peaks at a given frequency. Although DSC can be used to measure the glass transition temperature, DMA is more sensitive to thermal changes for amorphous materials such as asphalt binder where the content of crystallizable fractions is not significant. While the use of DMA in asphalt rheology has been limited, Lytton and co-workers evaluated the rate of damage accumulation in asphalt binder and mastic using DMA. Results of this test were found to correlate relatively well with mix performance against moisture damage in the field [13].

FTIR Spectroscopy

The functional group composition of the binders is examined using qualitative FTIR. Films of asphalts and rubber were cast from toluene on a NaCl plate and analyzed taking the blank plate as background. The extent of asphalt oxidation is correlated to the formation of carbonyl groups that appear in the FTIR spectrum around 1700 cm^{-1}.

OBJECTIVE

The initial objective of this research was to develop procedures and standards for applying GPC as an analytical tool to define the percentage amounts of polymer modifiers in polymer modified asphalt cements soluble in eluting GPC solvents. Part of this objective will address quantification of GPC solvent insoluble crumb rubber modifier present in crumb rubber modified binders for which a repeated solvent/non-solvent precipitation procedure will be developed. The second objective was the assessment of the extent of field aging of modified asphalt binders by using both GPC and rheological analyses.

SCOPE

This project was sub-divided into two phases: Phase I, development of procedures to define the content of polymers in polymer modified binders, and Phase II, to analyze plant polymer modified binders (and at various times field binders) by extracting and characterizing the asphalt liquid from core samples. Phase I will include (1) quantifying procedures and standards using different asphalt sources and different polymeric modifiers and (2) developing a solvent/non-solvent precipitation procedure to define the percentage of insoluble crumb rubber modifier present in crumb rubber modified binders. Phase II will perform binder tests based on chemical component analysis and binder characterization that will include (1) FTIR (Fourier transform infrared) spectroscopy measurements; (2) GPC (gel permeation chromatography) measurements; (3) DSC (differential scanning calorimetry), and (4) DMA (dynamic mechanical analysis) of mixture samples made of polymer modified binders.

METHODOLOGY

Asphalt binder materials were obtained from five major refineries A, B, C, D, and E in Louisiana. Different contractors used different refineries for their job mix formulation; therefore, for each job site, the samples were labeled using a letter assigned to the refinery by a number (e.g., A1 and A2) and to the contractor. Table 1 summarizes the details on the materials collected from original job mix formulations.

Table 1
Overview of road sites tested

Supplier Refinery	Contractor	Polymeric Additive used	Route, Location	Asphalt wt%mix	RAP wt%	Anti-stripping wt% mix	Binder Grade	JOB date
A1	D B	SOLPRENE	LA 26	3.9	0.8	0.6	70-22m	12/28/2007
A2		SOLPRENE	US 71				76-22m	08/15/2008
B1	Br	GLOBALPRENE	LA 18	4	0.7	0.6	76-22m	03/12/2008
B2	B B	GLOBALPRENE	LA 1	2.8	1.1	0.9	76-22m	03/27/2008
B3		LATEX	LA 1036				70-22m	11/04/2008
B4		GLOBALPRENE	LA 1036				70-22m	11/04/2008
B5		NO POLYMER	LA 1036				64-22	11/04/2008
C1	M	VECTOR	I 20		RAP		76-22m	04/15/2008
C2		VECTOR	US 190		No RAP		76-22m	10/15/2008
C3		CRUMB RUBBER DRY	I-12		No RAP			11/10/2008
C4		CRUMB RUBBER-WET	I-10		No RAP			10/15/2008
D1	DJ	CALPRENE	LA 15				76-22m	
E		Only Lab Voucher Samples Received						

Materials

Asphalt Binders

A listing of the sources of the asphalt binders tested is presented below:

- Asphalt and polymer modified asphalt materials were obtained directly from refineries (TANK). A group of 29 asphalt binder samples from five different refineries were analyzed and the results are summarized in Table 2 and Table 8.
- Binder specimens were extracted from samples collected at the contractor plant after drum mixing process (DRUM).
- Binder specimens were extracted from RAP mixtures used by the contractors when the samples were available (RAP).
- Binder specimens were extracted from HMA after transportation (TRUCK).
- Binders specimens were extracted from road cores with the following ages: new, 6 months, and 1 year.

Table 2

Asphalt binders provided by LADOTD asphalt materials laboratory

Refinery	Binder Grade	Test date	Re-test date	Tanks
D	64-22	4/10/2008	11/4/2008	1
D	70-22m	4/10/2008	11/4/2008	4
D	76-22m	4/10/2008	11/4/2008	4
C	64-22	4/10/2008	11/4/2008	6
C	70-22m	4/10/2008	11/4/2008	1
C	76-22m	4/10/2008	11/4/2008	4
A	64-22	4/10/2008	11/4/2008	2
A	70-22m	4/10/2008	11/4/2008	2
A	76-22m	4/10/2008	11/4/2008	1
E	64-22	4/10/2008	11/4/2008	1
E	70-22m	4/10/2008	11/4/2008	2
E	76-22m	4/10/2008	11/4/2008	1
B	64-22	4/10/2008	11/4/2008	N/A
B	70-22M	4/10/2008	11/4/2008	N/A
B	76-22M	4/10/2008	11/4/2008	N/A

Additional asphalt binder samples were obtained from the following sources:

1. Federal Highway Administration provided the following asphalt binder samples:
    a. An air blown asphalt (as original, RTFO and PAV samples, respectively)
    b. A PG 76-22 AC modified with linear SBS additive (as original, RTFO, and PAV samples, respectively)
    c. A PG 70-22 modified with linear SBS additive (as original, RTFO and PAV samples, respectively)
    d. A PG 64-40 modified with linear SBS additive (as original, RTFO, and PAV samples, respectively)
2. LADOTD provided road core samples and binders for polymer/crumb rubber content determination.
3. An asphalt R&D laboratory provided ACs modified with either styrene-ethylene-butadiene-styrene (SEBS) or styrene-butadiene-styrene (SBS).

Polymer Additives

Samples of the tri-block elastomeric copolymers used as additives were obtained from the refineries and analyzed by GPC. Each sample was dissolved in tetrahydrofuran (THF) and the chromatograms were obtained using the same conditions employed for asphalt analysis (*vida infra*). The commercial names of each polymer additive and a few critical characteristics are summarized below:

- **Calprene 411** – a Dynasol product (butadiene/styrene 70/30 %) in crumb form. The characteristics of the radial SBS tri-block elastomeric copolymer are as follows: 30% weight polystyrene (PS), 70% weight polybutadiene (PB) *[5]*. Molecular weight from GPC measurements around 650,000 that corresponds to an estimated 8,500 PB units and 1,800 PS units (900 PS units on each side of the PB chain) *[5]*.
- **Solprene 4301** - a Dynasol product. It is a linear block copolymer of styrene and butadiene, having 33% of styrene content, most of it forming a polystyrene block, which gives the polymer a thermoplastic behavior *[5]*.
- **Globalprene 3501** – a Taiwan product; no additional data available.
- **Butonal Latex** – a BASF product, which is a mechanically stable SBR latex. Properties: pH 10.0 – 11.0; Viscosity mPa s 1000 – 1500 (Brookfield RVT, Spindle #3, at 20 rpm) *Bound* styrene % 24; Glass transition temperature -53ºC (DSC) *[7]*.
- **Crumb Rubber** - local supplier, 30 mesh.
- **Kraton G1654h** - a linear tri-block copolymer based on styrene and ethylene/butylenes (SEBS), 31% styrene, and 63% reduced butadiene *[8]*.
- **Vector 2518-Ld** - a DEXCO Polymers product, which is a linear SBS tri-block copolymer containing 31% styrene, molecular weight > 10000 g/mol (estimated) *[9]*.

Methods and Procedures

Hot Toluene Extraction

A hot toluene extraction method was used to isolate asphalt binder from field samples. The apparatus used was a Soxhlet extractor (Figure 3). At the beginning of the project, the cores (6 in.x 4 in.) were cut into small pieces to an appropriate dimension, wrapped in a porous paper towel, and fitted inside the extractor. As the project advanced and a high volume of cores required extraction, the cores were just heated in an oven at 60°C for 15 minutes to facilitate the breakup of the asphalt matrix. The resultant loose material was allowed to cool for 30 minutes before packing into the extractor as described above and being subjected to hot toluene reflux for 24 hours (note: the RAP mixtures required as long as 72 hours to effect quantitative removal of the dark colored asphalt). A typical 1000-gram load was extracted with 2 liters of toluene. A nitrogen blanket was applied in order to avoid air oxidation. The resultant asphalt cement solution in toluene was cooled and allowed to stand at room temperature for at least 12 hours. After filtering to remove the fines, the filtrate was allowed to stand overnight to permit ultra-fine particles to settle before the solution was decanted. The solution was concentrated under vacuum at 0.1 mm Hg and 45°C to 65°C with a Büchi Rotavapor R200 apparatus (Figure 4). The residue was dried for 20 hours in a vacuum oven (Labline vacuum oven) first at room temperature for 15 hours, then at 50°C for 3 hours, and finally at 100-105°C for an additional 2 hours.

Figure 3
Soxhlet apparatus

Figure 4
Rotary evaporator

A thermo-gravimetric analysis (TGA) was performed on batches to assure that all the toluene was removed (less than 0.1 percent of the sample evaporated at temperatures below 180°C). Alternatively, the samples were heated to a constant weight *[5]*.

The efficacy of hot toluene as a solvent was confirmed by comparing total extraction of the binder from mixtures with the toluene/ethanol 85vol%/15vol% standard system by measuring extracted aggregate residual binder content in the aggregate residue *[9]*. Only 0.25 wt% of binder remained after using AASHTO method T 308 ignition at temperatures that reached the flashpoint of the binder in a furnace. The weight loss was recorded at temperatures lower than 100°C, which suggests that it can be attributed to the loss of very fine aggregates in the forced draft oven.

The porous paper towel used to wrap the loose mixture was weighed before and after extraction and solvent evaporation using an analytical balance; no difference was recorded. Also the towel was repeatedly washed with warm toluene, and the resulted solution was tested using GPC. No remaining asphalt composites were detected.

Alternate Extraction Procedures for Small Scale Samples

Gel permeation chromatography requires no more than 0.3 g asphalt binder samples/analysis. The researchers' work proved that a small binder sample can be retrieved from a mixture through the following steps:

1. Using a 28-oz (4.1"D x 4.7"H) covered tin-plated steel C-enamel can half filled with loose mixture, fill the can with toluene preheated at 70°C *[10]*.
2. Heat the can for 2 hours in oven at 60°C with occasional mixing,
3. Decant the hot asphalt solution and evaporate the solvent *in vacuo.* The residue can be diluted with THF for GPC injection or used directly for FTIR analysis.

Macro Scale Procedure

The small scale extraction could be extrapolated to larger quantities if more binder (> 500 g) is needed for additional analyses. The proposed procedure employs the following steps:

1. A 5 gallon covered solvent proof bucket should be half filled with loose mixture (~5 kg).
2. Toluene preheated to 70°C should be added in a ratio of 50:50 wt% and the bucket sealed.
3. The covered bucket should be inserted in a shaker to effect mixing (e.g., an automatic mixer used for HMA or an aggregate washer that takes aggregate samples and removes clay and other particles by gently agitating the specimen in a revolving drum until all particles are washed and separated).

4. After 1 hour, the soaking binder solution should be poured onto a wire-cloth sieves tower comprising of the sieves used for aggregate size distribution analysis (AASHTO M 92). It is suggested to use No. 325 (45 µm) and 450 (32 µm) in addition to the complete set of standard fine sieves No. 4 (4.75 mm), 8 (2.36 mm), 16 (1.18 mm), 30 (600 µm), 50 (300 µm), 100 (150 µm), and 200 (75 µm).
5. The sieve column should be washed with 300 mL aliquots of warm toluene until the effluent was colorless. The column effluent and the washings should be combined and the solvent evaporated *in vacuo* as described in the core extraction procedure.

Procedure to Detect Crumb Rubber Percentage in Asphalt Blends and Mixtures

First, a sample of crumb rubber to be blended with the asphalt liquid and containing the additives and fillers from the rubber processing should be extracted to determine percentage soluble rubber additives removed in hot toluene. The procedure was conducted as follows:

1. Weigh 1 - 10 grams of crumb rubber into a tarred beaker, record the sample weight as initial mass.
2. Add 50 mL of toluene preheated to 70ºC.
3. Prepare a vacuum filtration set-up, and record the weight of the filter papers before filtration.
4. After 2 hours of soaking, filter the toluene slurry via suction filtration.
5. Wash the extraction beaker a few times to completely remove crumb rubber from the walls.
6. If filter papers tend to clog, use as many filter papers as you need to collect the full quantity of insoluble crumb rubber.
7. Dry filter papers in vacuum oven for 3 hours at 80 ºC.
8. Record the total weight of filter papers, and subtract the initial weight of the filter paper. Record the difference value as the final mass of insolubles.
9. Compute the weight of the soluble by from the difference in weight: initial mass – final mass.

   The result can be expressed as weight percentage of soluble components carried by crumb rubber into mixture. Results showed this was an average of 13 percent for four different crumb rubber types that were tested.

Secondly, an unknown CRM asphalt modified liquid can be analyzed to determine the percentage of CR using the following the procedure:

1. Extract the asphalt binder using hot toluene extraction method or small scale extraction procedure presented in the previous sections.
2. Follow steps 3 to 9 presented above with a note for step 5: wash the crumb rubber on filter papers with cold toluene until total removal of the dark asphalt color occurs.

3. To the weight percentage of the crumb rubber extracted from asphalt binder, add the calculated percentage of soluble components based upon the crumb rubber extraction procedure described above.

In this study, the isolated insoluble CR in the CRM was 10 wt%. Correction for the solubles initially in the CR gives a total of CR added as 10 wt%+(10%x13%), i.e., 11.3 wt%. The procedure to detect percentage crumb rubber from an unknown core is different because hot toluene extraction of asphalt binder from the mixture, fails to remove insoluble crumb rubber from the aggregates' mass. Ignition method AASHTO T 308 for determination of asphalt content should be applied to assess the insoluble CR content as follows:

1. Divide a minimum 600-gram core sample into 2 parts: 400 and 200 grams
2. Extract asphalt binder and soluble part of CR using hot toluene (the 400 grams sample).
3. Determine mass loss after applying the ignition method on extracted aggregates and insoluble CR (insoluble CR % regardless to aggregates mass)
4. Subject the 200 gram sample aliquot to ignition test and record percentage mass loss (asphalt +CR %).
5. Calculate the weight percentage CR added to the asphalt binder.

A test of this procedure with the sample analyzed above yielded a result of 11.5% CR.

GPC Characterization

Gel permeation chromatography is a fast and reliable method to determine molecular weight (Mw) and molecular weight distribution of asphalt binders. The polymer, asphaltenes, and maltenes content in asphalt can be quantitated. Since unaged polymer molecules exhibit molecular weights 100 times more than those of asphalt molecules, they can be easily identified using this method.

GPC Instrument

The gel permeation chromatograph was equipped with an Agilent 1100 series autoinjector, a Waters 590 pump, and a Waters model 410 differential refractive index detector. The separation of the asphalt components was affected using Phenogel columns (10 µ packing, 300 x 7.8 mm) from Phenomenex, Torrance, CA, connected in series with a guard column. Seven different sets of columns with different porosities and two eluting solvents (THF and toluene) were evaluated to determine the most distinct separation between species. Researchers ascertained that eluting with THF through set 7 is the best combination of columns for GPC analysis at room temp.

The column set was calibrated with narrow molecular weight polystyrene (PS) standards using 3mg/15mL concentration in tetrahydrofuran (THF) (Table 4). The molecular weight distribution versus the elution volume was calculated and illustrated in the log/log scale plot using polystyrene standards (Figure 5). All asphalt and polymer samples were prepared at a concentration of 3% in THF and injected through 0.45 µm PTFE filters into 150 µL vials. Samples were eluted with THF at 1 mL/min at room temperature and the species concentration in the eluent was recorded using a differential refractometer.

Table 3
Number and size of GPC column used for each column set to optimize polymer/asphalt separation

Column size		50 Å	100 Å	500 Å	10^3 Å	10^4 Å	Linear MIX	
Mw size	Solvent	100-3K	500-6K	1K-15K	1K-75K	5K-500K	100-10,000K	Test time min
SET1	THF			1		1	1	35
SET2	THF			1		1	1	35
SET3	THF	1	1		1			45
SET4	THF		1	1	1	1		45
SET5	THF			1	2			45
SET6	THF				2	1		45
SET6	Toluene				2	1		50
SET7	THF			1	1	1	1	50

Table 4

Elution volume (Ve, mL) values for PS standards using column set 7

Mw	Ve	Mw	Ve	Mw	Ve
1820 K	22.33	137.9K	25.38	9.92K	31.97
1472K	22.58	96K	25.9	6.93K	33.18
990.5K	22.92	66.35K	26.6	4.92K	34.15
677.5K	23.35	52.4K	27.12	3.07K	35.52
523K	23.62	29.65K	28.58	1.94K	36.9
271.9K	24.43	19.88K	29.83	1.06K	38.67
218.8K	24.73	12.83K	31.2	0.58K	39.9

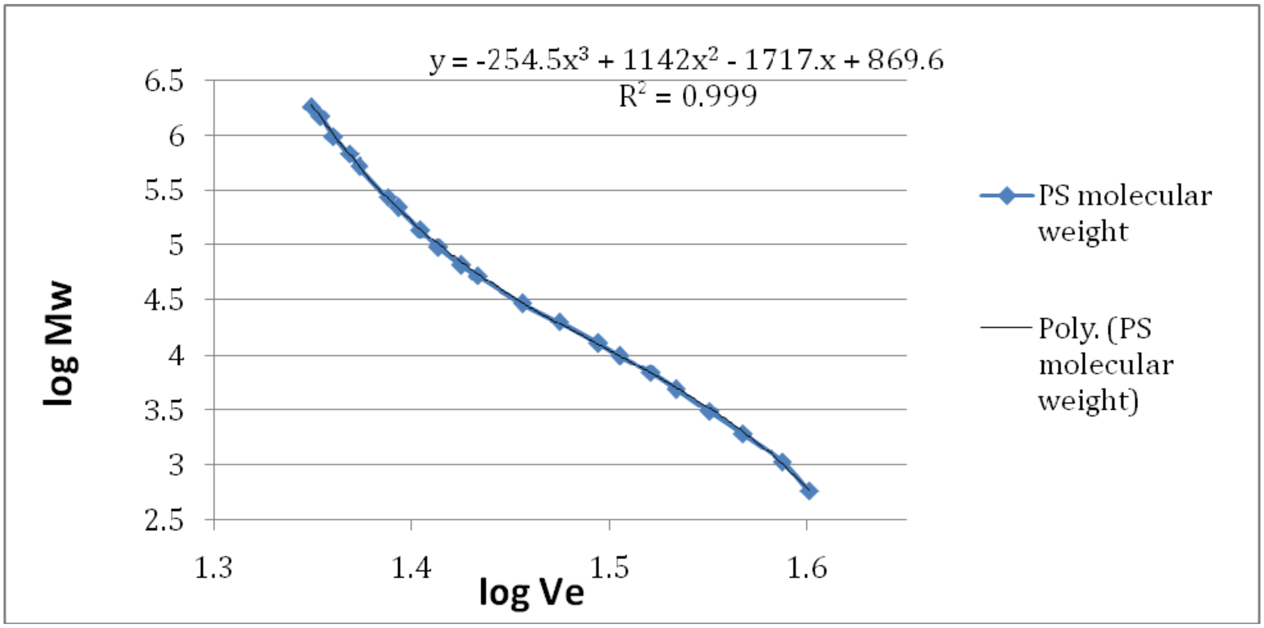

Figure 5
Calibration curve built based upon polystyrene standards (set 7)

Estimation of Components Insoluble in THF. All asphalt samples analyzed in this project contain a fraction of insoluble components. To estimate the THF insolubles, the following processing steps were applied:

- A 0.45µm syringe filter was weighed before passing the THF “solution” through it.
- A 150 µL vial was filled with filtered solution for further GPC injection.
- The same filter and additional pre-weighted filters were used to filter the remain THF solution.
- The filters were weighted after THF evaporation in the vacuum oven (1 hour, 50°C).
- The weight of residue was related to the initial sample weight to calculate the wt% of the insolubles.
- The value of percentage insolubles was used in GPC data computation as presented later in this report.

The estimation has shown typicality for the same PG grade asphaltic materials, the insoluble percentage in THF falls in the same range. A few typical samples are shown in Table 5.

Table 5
Percentages of insoluble species collected on 0.45µm filter

PG or aged RAP	Typical % insoluble THF
64-22, original	4%-5%
76-22 original	6-7%
76-22, core new route	10-11%
RAP	7-10%
Source	Atypical
B1 refinery	18%
LA 18 new	23%
Latex modified asphalt	0.2-2%

Rheological Measurements

Rheological measurements were made using a dynamic mechanical analyzer AR2000 rheometer (TA Instruments Inc., Waters Corp., New Castle, DE), which was set to work in Dynamic Shear mode. This instrument is specially designed for characterization of soft materials. The basic DSR test uses a thin asphalt binder sample sandwiched between two plates. The lower plate is fixed while the upper plate oscillates back and forth across the sample at 1.59 Hz to create a shearing action. These oscillations at 1.59 Hz (10 radians/sec) are meant to simulate the shearing action corresponding to a traffic speed of about 90 km/hr (55 mph) (Roberts et al., 1996). The steel plates have circle geometry with diameter of 25 mm (used for original materials) and 8 mm (for aged materials) with a test gap between them of 1 and 2 mm respectively. A disk of asphalt with equal diameter to the plates was prepared by pouring into a standard silicon mold. The molded disk was placed between the oscillating and fixed plates of the rheometer The excess asphalt was removed by trimming with a hot spatula. Regardless of the standard procedure, (AASHTO TP5) a trimming gap was first set at 1.05, respectively 2.1 mm gap, and then the upper plate was set for the testing gap. An environmental temperature control (ETC) oven allowed a precise control of temperature within 0.1°C. The test procedures specified a 30 minute temperature equilibration time; a controlled strain of 12% for original binder, 10% for RTFO samples and 1% for PAV materials; and a constant 10 rad/s frequency.

An ARES rheometer was used for dynamic mechanical analysis of the selected asphalt binders in order to determine the glass transition temperature. The following test parameters were used: torsion (twisting) in a cooling mode; sample dimensions: 3 mm x 13 mm x15 mm, cooling rate: 1°C /min, frequency: 1Hz, and sinusoidal cyclic strain with an amplitude of 1 percent.

Differential Scanning Calorimetry. The presence of crystalline species (considered mostly as paraffinic maltenes) was determined using DSC for selected asphalt binders These measurements were conducted using a TA 2920 MDSC V2.6A module at the following testing conditions: 5-10 mg sample and a heating rate of 2°C /min with a modulation program of 0.5°C at each 0.4 minute.

DISCUSSION OF RESULTS

Gel Permeation Chromatography

Gel permeation chromatography is a form of size-exclusion chromatography. The smallest molecules pass through all the bead pores, resulting in a relatively long flow path while the largest molecules flow through only the larger pores, resulting in a relatively shorter flow path. The chromatogram shows detector response (differential refractive index, DRI) versus time or elution volume (Ve). The highest molecular weight molecules appear first on the chromatogram following by medium and eventually low molecular weight species. The organic solvent used should disturb the associations as little as possible, exhibit a refractive index significantly different from the analyte, and have a relatively low-boiling point. For this study, THF was the solvent of choice. GPC chromatographs obtained using toluene as the solvent exhibited lower resolution (see Table 3, set 6 row) and the differential refractive index between toluene and asphalt components was very small. Using the calibration curve (Figure 5), the results from GPC elution volumes were correlated with the macromolecular weights of the compounds. It was expected that, during oxidative aging, the polymer molecules from PMAC would be linked through stable chemical bonds, e.g., covalently bonded, crosslinked "gels" that are not soluble in THF. It is also possible that some highly aggregated asphaltenes are insoluble in THF. Insoluble species and gels were precluded from entering the columns through filtration through a short guard column. Since GPC measures the soluble components only, the final calculation of the binder composition must be corrected for the insoluble component content.

The GPC studies presented in this chapter concern:

a. the development of a standard procedure for using GPC as an analytical tool to define the percentage amounts of polymer modifiers in polymer modified asphalt binders soluble in eluting GPC solvents
b. the assessment of the extent of oxidative aging of modified asphalt binders in the field
c. the differences in molecular weight distribution of asphalt materials from a few major suppliers

Based on more than 900 chromatographs analyzed in this study, the following molecular weight regions were defined: very high molecular weight (VHMw polymeric species) 1000-300K, high molecular weight (HMw polymeric species) 300-45K, medium molecular weight (MMw aggregated asphaltenes and oxidized polymer species 45-19K), asphaltenes (19-3.5K), and maltenes (3.2-0.1K). A typical chromatogram is shown in Figure 6. For each of these regions, a relative change of integrated area during oxidative aging was computed.

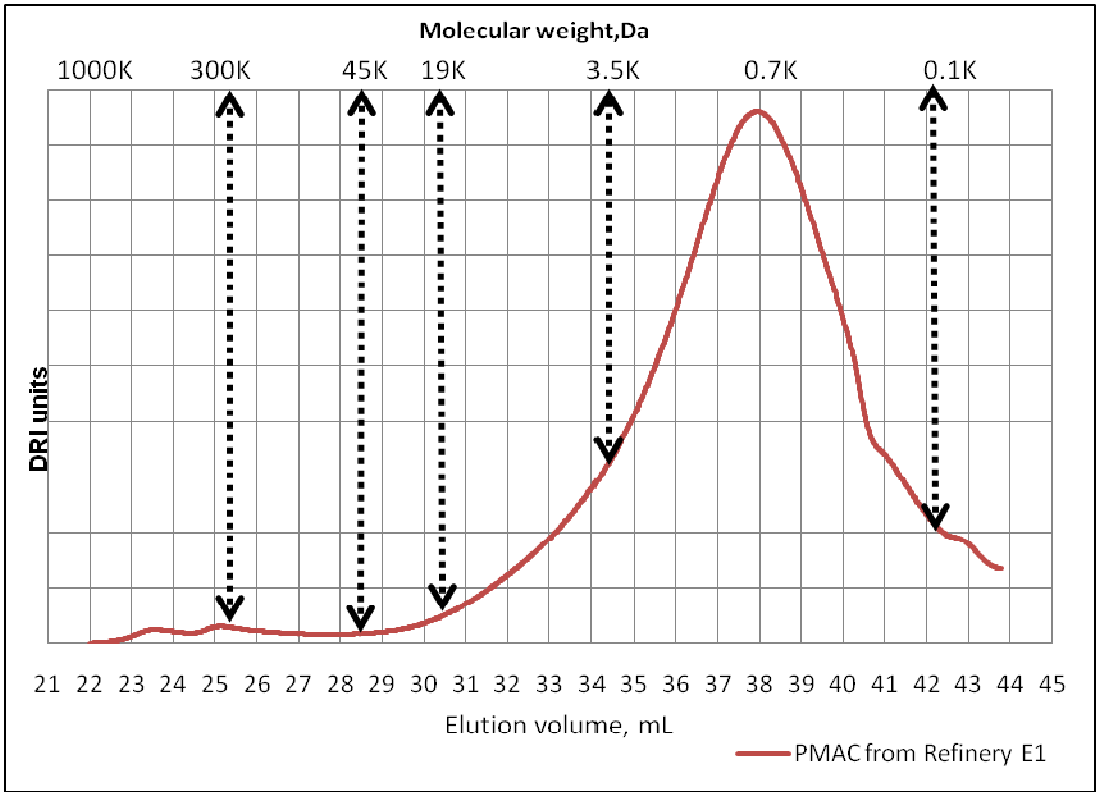

Figure 6
Regions of a PMAC GPC chromatograph showing the relationship between elution volume and molecular weights values, based on calibration curve

Fingerprint Database Using GPC Analysis

The shape of the GPC curve is similar to a finger print, particularly in the polymer molecular weight region. A fingerprint database of GPC curves was compiled from the chromatograms of 29 different asphalt binder samples, covering PG grading 76-22m, 70-22m, and 64-22 from five major refineries (the same refineries providing asphalts used for the routes examined in the investigations). The area under the defined regions of the GPC chromatograms is directly related to the weight percentage of each component. The relative concentrations of each component in virgin asphalt samples can be considered the baseline data for that particular asphalt source. Examination of samples from original materials as well as the corresponding RTFO and PAV aged samples allowed the compilation of baseline compositions. Rheological data for these samples were provided by LADOTD materials laboratory, so a relationship between asphalt composition and it's rheology can be considered. An example of this baseline data is compiled in Table 6. A consistency in the molecular weight distributions for the same PG grading from the same supplier was observed. After 6 months the test was repeated and the results were similar.

Overall, the average molecular distribution of asphalt materials (Table 7) from the five refineries fell in the following ranges: very high molecular weight (VHMw, 1000-300K Daltons, KDa), high molecular weight (HMw, 300-45KDa), medium molecular weight (MMw, 45-19KDa), and asphaltenes (19-3KDa and maltenes (3-0.2KDa). The total amount of high molecular weight components defined a molecule with molecular weights from 1000-19KDa is called the sum. These high molecular weight components make a significant contribution to the asphalt rheology.

Table 6
Example of baseline data on distribution of asphalt components

GPC		VHMw	HMw	MMw	Sum	Asphaltenes	Maltenes	Total
Run No.		1000-300K	300-45K	45-19K		19-3K	3-0.2K	
C	D1 70-22M	0.5%	0.4%	0.3%	1.2%	16%	83%	100%
10	D1 70-22MRTFO	0.3%	0.4%	0.5%	1.2%	16%	82%	100%
118	D1 70-22M PAV	0.3%	0.3%	0.5%	1.1%	19%	80%	100%
CD	D1 70-22M	0.5%	0.2%	0.2%	0.9%	16%	83%	100%
70	D1 70-22MRTFO	0.3%	0.3%	0.3%	0.9%	16%	83%	100%
95	D1 70-22M PAV	0.2%	0.3%	0.4%	0.8%	18%	81%	100%
L	D1 70-22M	0.3%	0.4%	0.3%	1.1%	15%	84%	100%
92	D1 70-22M RTFO	0.2%	0.4%	0.5%	1.0%	18%	81%	100%
2	D1 70-22M PAV	0.1%	0.3%	0.5%	1.0%	20%	79%	100%
X	D1 70-22M	0.3%	0.4%	0.3%	1.1%	14%	85%	100%
71	D1 70-22M RTFO	0.2%	0.3%	0.5%	0.9%	17%	82%	100%
98	D1 70-22M PAV	0.2%	0.2%	0.6%	1.0%	19%	80%	100%

Table 7
Distribution of components in original asphalt binders

		VHMw	HMw	MMw	Sum	Asphaltenes	Maltenes	Total
	PG	1000-300K	300-45K	45-19K	1000-19K	19-3K	3-0.2K	
A	64-22	0.0%	0.0%	0.0%	0.0%	15%	85%	100%
A	70-22M	0.2%	0.6%	0.5%	1.3%	15%	84%	100%
A	76-22M	0.6%	3.0%	0.7%	4.3%	14%	82%	100%
B	64-22	0.0%	0.0%	0.0%	0.0%	19%	81%	100%
B	70-22M	0.1%	1.2%	0.6%	1.9%	17%	81%	100%
B	76-22M	0.3%	1.0%	0.8%	2.1%	16%	82%	100%
C	64-22	0.0%	0.0%	0.0%	0.0%	16%	84%	100%
C	70-22M	0.0%	0.5%	0.8%	1.3%	17%	82%	100%
C	76-22 M	0.1%	1.3%	1.2%	2.7%	17%	81%	100%
D	64-22	0.0%	0.0%	0.0%	0.0%	16%	84%	100%
D	70-22M	0.3%	0.4%	0.3%	1.1%	15%	84%	100%
D	76-22M	0.1%	1.1%	1.3%	2.5%	14%	83%	100%
E	64-22	0.0%	0.0%	0.1%	0.0%	13%	87%	100%
E	70-22M	0.1%	1.0%	0.9%	1.9%	14%	84%	100%
E	76-22M	0.3%	2.6%	0.8%	3.7%	12%	85%	100%

A graphical presentation of the high molecular weight component data compiled in Table 7 is presented in Figure 7 and the corresponding data for combined polymer and asphaltenes are shown in Figure 8. Note that the distribution of polymer molecular weights varies based upon the selection of the polymeric modifier.

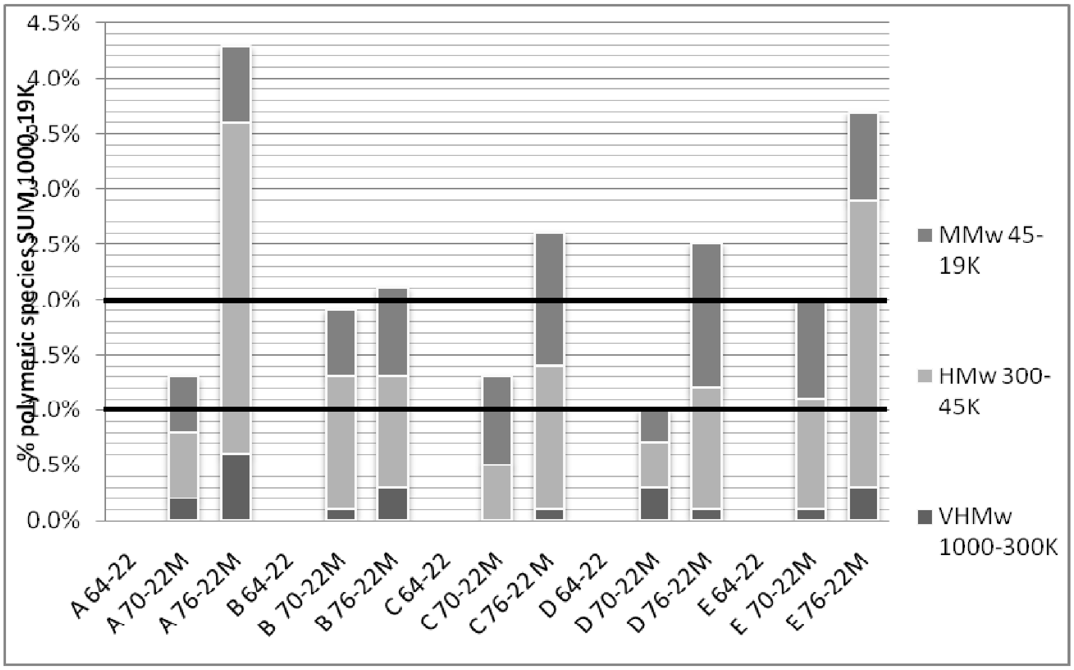

Figure 7
High molecular weight component content of original asphalts from different refineries

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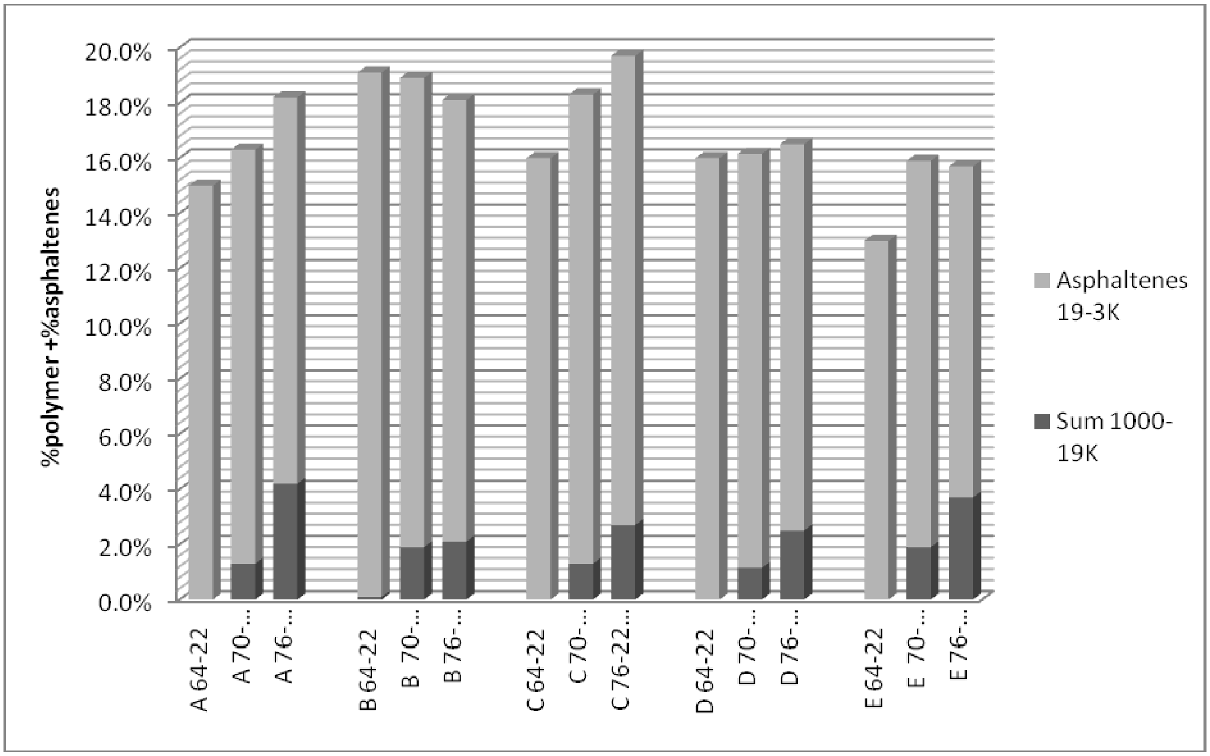

Figure 8
Visible differences in polymer and asphaltene content in asphalts from different refineries

In addition to samples of asphalt and polymer modified asphalt binder, the researchers' fingerprint database covers the following types of polymers: Globalprene SBS linear, Solprene SBS linear, Kraton SEBS, and Calprene SBS-radial. Figure 9 shows the GPC traces for each of the polymers used by Louisiana refineries. The differences in shape and molecular weight distributions characteristics of radial and linear polymers can be a useful tool in qualitative identification of the polymer type used in addition to quantitative GPC evaluation (Table 8).

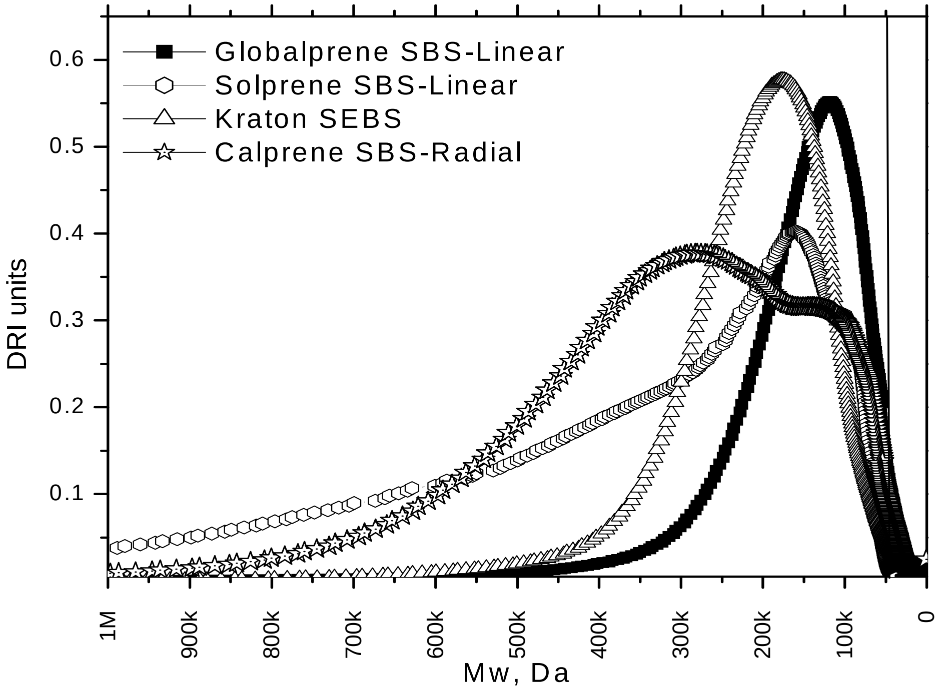

Figure 9
Continuous molecular weight distribution of SBS polymers used by Louisiana refineries

Table 8
GPC analysis of triblock polymer additives

		VHMw	**HMw**	**MMw**	**Sum**	**LMw**	**vLw**
GPC run number	Polymer additive	**1500-300K**	**300-45K**	**45-19K**		**19-3.5K**	**3.5-0.2K**
129	Globalprene SBS-L	4.7%	70.6%	16.9%	92.1%	4%	4%
435	Solprene SBS-L	20.2%	77.2%	2.2%	99.7%	0%	0%
112	Calprene SBS-R	34.2%	52.1%	8.7%	95.0%	2%	3%
116	Kraton SEBS	3.6%	88.0%	3.7%	95.4%	2%	2%
142	Vector SBS	0.5%	73.9%	21.9%	96.3%	3%	1%
26	Latex SBS	27.4%	56.0%	6.7%	90.2%	8%	2%

Based upon the review of asphalt liquids in the study, researchers determined that the suppliers examined in this study keep their formulations constant. The suppliers are using different types of SBS polymer and different percentages. However to meet the requirements for a PG 70-22, researchers observed that at least 1 wt % up to 1.98 wt % polymer is added (Figure 7). To achieve PG 76-22, a minimum of 2 wt% polymer is added. The actual percentages of polymer vary as a function of the initial asphaltenes content and the type of polymer used. The GPC method can identify the type of polymer used as well as the percentages of polymer and asphaltenes present.

Evaluation of Binder Samples Employed in the Field

This study covers several contractors using various PG grades achieved with different types of polymer additives based upon the refinery. For each road, a voucher sample of the asphalt binder was obtained from the storage tank containing the asphalt liquid used to prepare the HMA by mixing with aggregates. At the plant, contractors mix PMAC liquids from tanks with aggregates and RAP. HMA samples were collected from the drum mixers, the transporter truck, and core samples of the new pavement. After hot toluene extraction, samples were analyzed through GPC and the results compiled in Table 9. The data show that minimal oxidative aging occurs during polymer mixing and PMAC storage.

Table 9
Percent of components in PMAC samples from tank, drum mixer, transportation, and field core

		VHMw	**HMw**	**MMw**	**Sum**	**Asphaltenes**	**Maltenes**
		1000-300K	**300-45K**	**45-19K**	**1000-19K**	**19-3.5K**	**3.5-0.2K**
A1	Tank for LA26	0.2%	1.1%	0.5%	1.9%	18%	80%
A1	LA 26	0.2%	1.5%	1.4%	3.1%	25%	72%
A2	Tank	0.2%	1.2%	1.0%	2.4%	18%	79%
A2	RAP for US 71	0.0%	0.7%	2.2%	3.0%	27%	70%
A2	us 71	0.0%	0.4%	1.9%	2.3%	22%	76%
B1	Tank	0.2%	1.2%	1.0%	2.4%	17%	81%
B1	Rap for LA 18	0.0%	0.1%	1.5%	1.6%	28%	70%
B1	LA 18 after drum	0.2%	1.3%	1.6%	3.1%	22%	75%
B1	LA 18 after truck	0.1%	1.3%	1.6%	3.1%	21%	76%
B1	LA18 road core	0.0%	1.2%	2.3%	3.5%	26%	70%
B2	Tank for LA 1	0.3%	1.1%	1.2%	2.6%	18%	79%
B2	rap for LA 1	0.0%	0.5%	2.3%	2.8%	27%	70%
B2	LA 1 after drum	0.1%	1.0%	1.9%	2.9%	24%	73%
B2	LA 1 after truck	0.1%	1.0%	1.9%	2.9%	24%	73%
B2	LA1 road core	0.1%	1.0%	1.8%	2.8%	24%	73%
C1	Tank	0.1%	2.1%	0.8%	3.1%	18%	79%
	No RAP						
C1	US 190	0.1%	2.0%	1.5%	3.6%	21%	75%
C2	Tank	0.0%	1.5%	2.0%	3.5%	17%	79%
C2	rap for I-20	0.0%	0.2%	2.3%	2.5%	30%	67%
C2	I-20	0.1%	1.3%	1.9%	3.2%	23%	74%
D	Tank	0.7%	0.8%	0.6%	2.1%	14%	84%
D	Rap for LA 15	0.0%	0.2%	1.1%	1.3%	24%	74%
D	LA 15 after drum	0.5%	0.7%	1.0%	2.3%	19%	79%
D	LA 15 after truck	0.4%	0.8%	1.0%	2.2%	17%	81%
D	LA 15 road core	0.2%	1.2%	0.9%	2.3%	20%	77%

RAP Impact

In fresh pavements, the addition of RAP does not have a significant impact on the physical properties (Table 10). The data show a good correlation between laboratory RTFO prediction for G*/sinδ and field only for the project without RAP [refinery C1 route; no differences were found between the samples collected after the drum mixer process, truck transportation, and a core from the new pavement (after hot roller)]. The noticeable difference is between tank samples and road samples, respectively. An increase in polymer content and asphaltenes content can be attributed in the addition of RAP. From the first project on route LA 26 having A1 supplier, researchers learned that it is a difference in high molecular weight components between the new road and tank binder. The only difference in molecular weight distribution for a given job was observed after drum mixing. The RAP added in mix process (around 20% RAP) has the impact presented in the Table 9.

The RAP materials tested and used on the roads have 1-2% medium molecular weight components and 24-30% asphaltenes and present an average of 7% insoluble species in THF. The addition of the new RAP species has a minimum impact on the polymer size area compared to the impact on asphaltene area. The asphaltene content increased between 6-8%.

US 190 road has no RAP added; during the oxidative process of mixing only a 3% increase in asphaltenes was recorded. In this case, the source of asphaltenes was aggregation promoted by oxidation. Assuming similar contribution to the asphaltene content due to oxidation, asphaltene levels higher than 3% are US 190). Adding RAP with 1-2% polymeric content allows the mixture to retain the G*/sinδ values observed for an original material. The new, fresh road that contained RAP is original type asphalt from GPC analysis, DSR data, and MSCR results (presented later in this report). These results suggest that the addition of polymer modified RAP is beneficial for the fresh road.

Table 10
Rheological measurement for PMAC extracted from field core samples

		G*/sinδ	Temp	Job mix
		kPa	°C	formulation
				PG
D LA 15	Refinery D	1.391	76	
D LA 15	Tank	1.044	76	
D LA 15	Rap for LA 15 road	3.68	80	
D LA 15	Drum	1.648	76	
D LA 15	Tank RTFO	1.72	76	
D LA 15	Drum RTFO	2.3	80	
D LA 15	road core	1.483	76	76-22
B1 LA18	Refinery B	1.21	76	
B1 LA18	RAP for LA 18	2.2	88	
B1 LA18	road core	1.6	76	76-22
C1	Tank	1.65	76.00	
C1	Tank RTFO	2.87	76.00	
C1	road core -no RAP	2.40	76.00	76-22
A2	road core	1.22	76	76-22
C2	road core	1.69	76	76-22

Time Impact

Samples were cored from specific testing areas on designated routes, and the asphalt liquid was extracted with hot toluene and analyzed using GPC after 1 year in the field. The changes in fraction weights for the arbitrary regions selected were monitored and the data are presented in Table 11. In selected cases, after 6 months in service, minimal changes occurred as shown in the data. Further six month coring was deemed unnecessary.

Table 11
Changes occurring during 1 year in % weight fraction of asphalt components

Route	Age	**VHMw**	**HMw**	**MMw**	**Sum**	**Asphaltenes**	**Maltenes**
		1000-300K	**300-45K**	**45-19K**	**1000-19K**	**19-3.5K**	**3.5-0.2K**
LA 26	new	0.2%	1.5%	1.4%	3.1%	25%	72%
LA 26	6 months	0.0%	0.9%	1.5%	2.5%	22%	76%
LA 26	1 year	0.0%	0.7%	1.7%	2.4%	22%	76%
US 71	new	0.0%	0.4%	1.9%	2.3%	22%	76%
US 71	1 year	0.0%	1.3%	1.8%	3.1%	25%	72%
LA 18	new	0.0%	1.2%	2.3%	3.5%	26%	70%
LA 18	1year	0.1%	1.6%	3.8%	5.5%	22%	73%
LA 1	new	0.1%	1.0%	1.8%	2.8%	24%	73%
LA 1	1 year	0.1%	1.3%	2.5%	3.9%	21%	75%
US 190	new	0.1%	2.0%	1.5%	3.6%	21%	75%
US 190	1 year	0.3%	1.6%	1.6%	3.5%	13%	84%
LA 15	new	0.2%	1.2%	0.9%	2.3%	20%	77%
LA 15	6 months	0.2%	1.1%	1.1%	2.4%	22%	76%
LA 15	1 year	0.2%	1.3%	2.2%	3.6%	16%	80%

After the 1st year, the results varied according to location as follows:

- LA 26 route – the aging process affected polymeric regions. The polymer became insoluble in THF due to the formation of cross linked species. Around 0.6% from total initial polymer is not seen by GPC analysis (20% of the polymer is cross linked). Around 10% of the polymer was degraded via cleavage reaction resulting in 0.3% increase in medium molecular weight region (short polystyrene chains). No changes were noticed in the asphaltenes and maltenes region. The results exhibited by asphalt binder extracted from route LA 26 were expected. Researchers cored this road only in winter time (January), while all the other roads were cored in warmer seasons (July and August). Perhaps this was the reason the road behaved well. Alternatively, the asphalt binder from this refinery had good and sufficient maltenes species to absorb the RAP impact. Asphalt binder provided by refinery A always exhibited a low asphaltenes content and high maltenes content. The insolubles in THF did not increase significantly after 1 year (~1%).

- No RAP was added to the mix used to pave US 190. After 1 year, a decrease of asphaltenes species with molecular weights ~10 KDa was observed. There was a slight increase in the 5 KDa asphaltenes region, and a significant increase in the maltenes content in the 3-3.5KDa region. Temporary asphaltene aggregates formed during the drum mixing process dissociated after 1 year, reaching the same distribution shown by refinery PMAC (Figure 10).

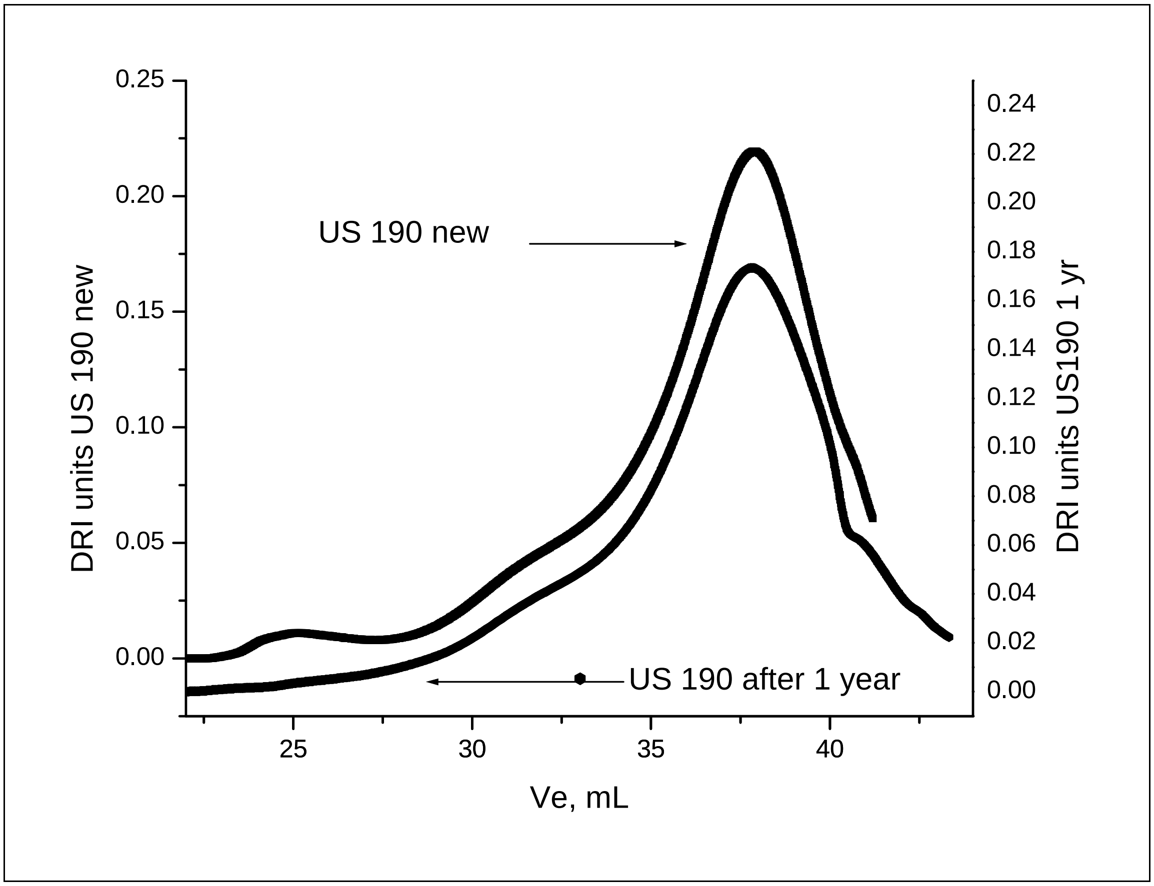

Figure 10
GPC chromatogram of binder from US 190 (no RAP) after 1 year in the field

- LA 15, LA 1, and LA 18 were transformed after 1 year. A visible increase in MMw region was observed around 38 KDa. The shape of the GPC traces changed (e.g., LA 18 after 1 year as shown in Figure 11). All the job formulations for these routes included RAP. The percentage of mix not passing 0.45 µm filter for these samples reached 23%, showing the potential presence of complexes formed between the polymer chain and asphaltenes.

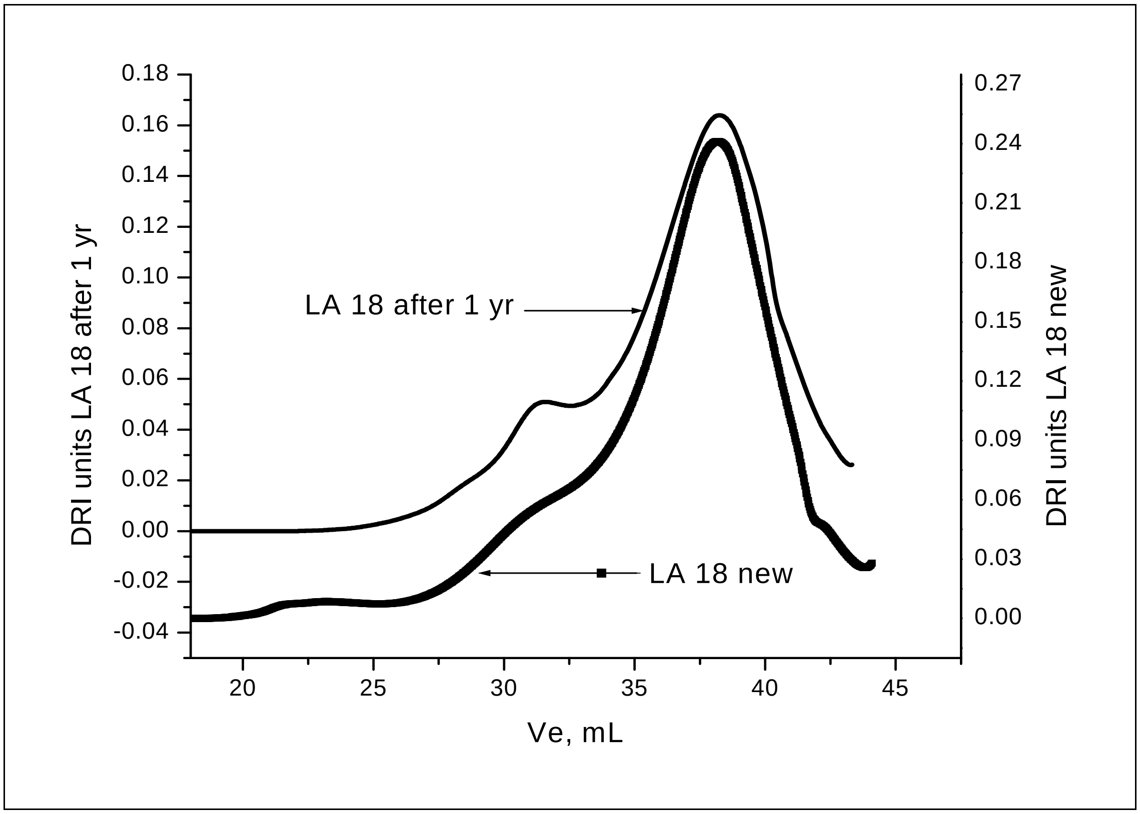

Figure 11
GPC chromatogram of binder from LA 18 after 1 year in the field

Crumb Rubber (CR) Asphalt Mixtures

One of the purposes of this study was to apply GPC methodology to all types of asphalt materials and to consider possible GPC limitations. Besides asphalt and SBS polymer modified asphalt, this study explored the possibility to analyze crumb rubber modified (CRM) and Latex binders.

There are two different ways to add CR to asphalt binders, i.e., wet and dry processes. The base asphalt graded PG 64-22 was provided by the same refinery (code C). A wet process was used to prepare the asphalt mix for route I-10 by first mixing CR (in proportion of 11.5%) with the asphalt liquid. The product named FLEX was added to the aggregate in a drum mixer. A dry process was used on a test region of route I-12. A CR mixture was previous prepared using 12% 80 mesh CR mesh, Vestenamer, and Gilsonite. The formulation of this job asked for the addition of asphalt binder, aggregates, and CR mixtures simultaneous in the drum mixer.

To understand better how GPC analysis can be used for CRM asphalts, each component part of the final binder was dissolved in THF, 3% concentration, and the solution was passed through a 0.45 μm filter. The percentage not passing the filter was computed. To obtain a 3% concentration, CRM in THF, 0.3 g of CRM were used, and the percentage insoluble in THF was computed to be 10% (the same value as when we used a much larger sample). By adding the quantity soluble in THF, the final result was 11.3% CR (close to 11.5% formulated for I-10). In the following tables, the GPC analysis findings are presented:

Table 12
Asphalt-CRM components produced by a dry process for Route I-12

GPC		**VHMw**	**HMw**	**MMw**	**CR**	**Sum**	**Asphaltenes**	**Maltenes**
Run No.		**1500-300K**	**300-45K**	**45-19K**	**%insoluble**		**19-3K**	**3-0.2K**
C	64-22	0.0%	0.0%	0.0%		0.0%	16%	84%
315	I-12	0.1%	1.1%	4.2%	11%	16.4%	25%	58%
198	Vestenamer	5.5%	53.7%	28.8%		88.1%	9%	3%
199	CR	0.0%	0.1%	0.9%	85.0%	86.1%	6%	8%
22	Gilsonite	0.0%	0.0%	0.0%		0.1%	49%	51%
107	Gilsonite +CR	0.1%	2.0%	5.5%	53.0%	60.6%	25%	14.4%

Molecular distribution of extracted binder from I-12 mixture shows the presence of around 5% Vestenamer, 10% Gilsonite, and 1.1% soluble CR . The 11% insoluble CR should be added to these components. High temperature, rheological measurements showed that both mixes meet the state requirements, respectively, at 82°C. MSCR tests revealed that CRM asphalt extracted from route I-10 meets the specification (the results are not included in this report).

Table 13
Asphalt-CRM components produced by a wet process for Route I-10

GPC		**VHMw**	**HMw**	**MMw**	**% insoluble**	**Sum**	**Asphaltenes**	**Maltenes**
Run No.		**1000-300K**	**300-45K**	**45-19K**	**CR**		**19-3.5K**	**3.5-0.2K**
449	I-10 CR plant	0.0%	0.5%	0.7%	10.0%	11.2%	17%	72%
434	solubleCR + gilsonite I-10	0.2%	2.8%	5.9%		8.8%	27%	64%
434	CR for I10 soluble hot Toluene	0.2%	2.9%	8.1%		11.2%	26%	63%

Analysis of Latex Modified Binder

When a problem case was brought to the testing lab, researchers had the opportunity to apply the GPC method to a latex modified asphalt binder by testing Route LA 1036. The cores came for confirmation that the contractor added the right amount of latex to the mixture, as the road after 2 months contained higher air voids (10%) on areas where the latex additive was used, compared to areas where SBS was the additive to the same base asphalt binder. The latex project was added to the scope. For the specific sections on LA 1036, researchers can comparatively analyze aging of a PG 64-22, PG 70-22 (SBS additive), and PG 70-22 (latex additive) from the same refinery (code B). The data in Table 14 show that the appropriate amount of latex is present in the mix.

To understand the problem, laboratory mixtures were prepared using PG 64-22 asphalt at different mixture temperatures. The test was conducted over a period of 3 weeks. Periodically, samples were removed and analyzed using GPC. No difference in the samples at different mixing times could be detected. The PG 64-22 asphalt binder had a high asphaltenes content leading to a rather stiffer mix. The job was done in cold weather (November), so the fully expected packing did not take place. As the latex was present in the right amount, researchers recommended a retest for air voids sometime in spring or summer. Indeed, the retested road in the summer time exhibited normal air voids content. Currently, the road is in good shape.

Table 14
Analysis of latex containing cores from LA 1036

GPC		VHMw	HMw	MMw	Sum	Asphaltenes	Maltenes
sample ID		1000-300K	300-45K	45-19K	1000-45K	19-3.5K	3.5-0.2K
433	LATEX for LA 1036	49.9%	50.1%	0.0%	100.0%	0%	0%
460	LA 1036 PG64-22	0.0%	0.0%	0.0%	0.0%	17%	83%
446	LA 1036 (latex)	0.4%	0.5%	1.1%	2.0%	23%	75%
23	LA 1036 (latex) after 4 mo	0.4%	0.6%	0.9%	1.9%	21%	77%
18	LA 1036(latex) after 8 mo	0.2%	0.2%	1.2%	1.6%	17%	82%
63	LA 1036 PG70-22(SBS)	0.1%	0.9%	0.7%	1.8%	20%	78%

DMA and DSC Results

Differential Scanning Calorimetry

DSC is widely used for determination of thermal transitions brought about by the first order transitions, such as melting and crystallization of crystallizable species. Glass transition, T_g, credited as a second order phenomenon taking place in the amorphous region of the sample, can be also defined by DSC, but it depends largely on the nature of the material and its content of crystallizable fractions. By allowing the temperature to oscillate in a sinusoidal fashion, a clear distinction can be made on the short time scale of the transition between non-reversible phenomena, such as the first order transitions and reversible glass transition *[11, 12]*.

Dynamic Mechanical Analysis

The DMA technique allows characterization of the variation of the dynamic complex modulus (E*) and its components (E', E", and tanδ) with temperatures. In this test, a beam sample is subject to a cyclic, torsional strain-controlled loading while the temperature is linearly decreased until failure occurs. The glass transition can be detected using DMA by identifying the temperature at which E" peaks at a given frequency. Although DSC can be used to measure the glass transition temperature, DMA is more sensitive to thermal changes for amorphous materials such as asphalt binder where the content of crystallizable fractions is not significant. While the use of DMA in asphalt rheology has been limited, Lytton and co-workers evaluated the rate of damage accumulation in asphalt binder and mastic using DMA. Results of this test were found to correlate relatively well with mix performance against moisture damage in the field *[13]*.

Three asphalt binders were selected for laboratory characterization using differential scanning calorimetry and dynamic mechanical analysis. The selected asphalt binders exhibited contrasting rheological behaviors: low ductility (25°C) and low stiffness (-12°C) (asphalt binder B3) and high ductility at intermediate temperatures and high stiffness at low temperatures (asphalt binders B4 and B5). A typical modulated DSC curve is shown in Figure 12 for asphalt binder B4 (original). This curve can be used to calculate enthalpies of transitions by integrating the peak corresponding to a given transition and to determine crystallization events at a given temperature. This information is very valuable since the percentage of crystallizable species is an indicator of brittle behavior at a given temperature. The DSC content of crystallizable species was determined below and above 25^{o}C by referring the enthalpy of sample melting (determined as an endothermic transition on the heat flow plot) to the melting enthalpy of 100% crystalline polyethylene (293 J/g) and the content of LMW fraction (maltenes) previously determined from GPC. The glass transition temperature of the selected binders was determined using DMA. The glass transition temperature is identified by the temperature at which E" peaks when plotted against the test temperature. Typical examples of this plot is presented Figures 13 and 14 for binders B4 (RTFO residue) and I (PAV residue), respectively. In all tested cases, the sample broke right after passing the glass transition temperature, confirming that the material behaves like a crystalline-brittle solid.

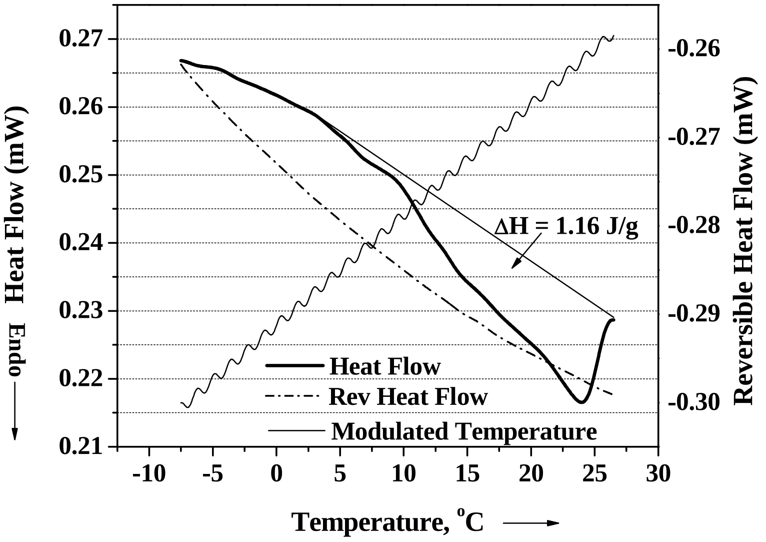

Figure 12
Modulated DSC analysis of asphalt binder B4 (original)

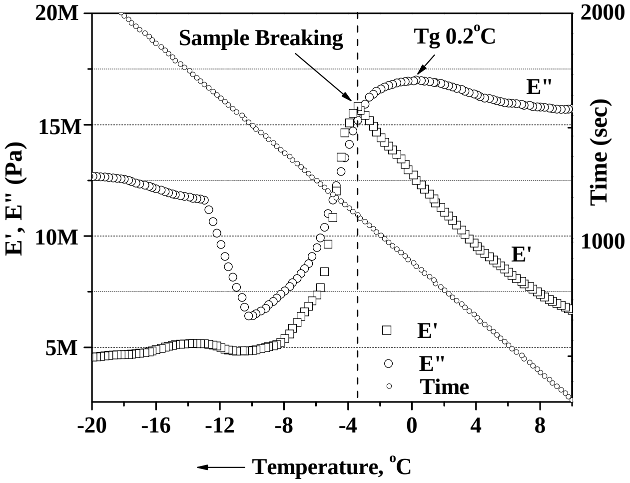

Figure 13
DMA analysis of asphalt B4 (RTFO residue) showing the sample breaking just below the glass transition temperature

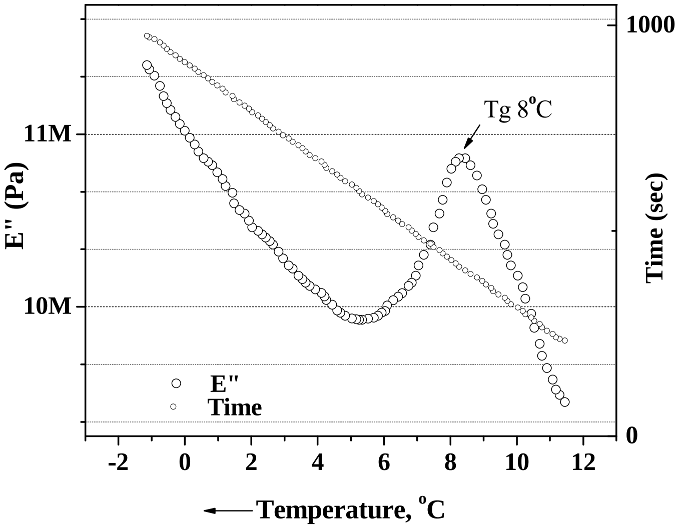

Figure 14
Glass transition temperature (DMA analysis) of binder B5 (PAV residue)

The content of crystallizable species of selected asphalt binders determined by DSC is presented together with the glass transition temperature determined by DMA in Table 15. The crystalline fractions melting above 25°C presented in this table have an adverse effect on the sample ductility at intermediate temperatures since these fractions act as brittle components. The ductility of asphalt binder B3, lower than that of binders B4 and B5, might be explained by its higher content of crystalline fractions melting above 25°C (Table 15). On the other hand, the crystalline fractions melting below 25°C may have a negative effect on the sample stiffness at low temperatures. This is the case of asphalt binder G (PAV-residue) with 0.86% LMW crystalline fractions melting below 25°C, which was higher than for asphalt binder D in which no melting of crystalline species has been detected in the same temperature range. However, the stiffening of asphalt binders at low temperatures is a complex phenomenon in which paraffinic (maltene) crystallization might only have a reduced role. This is evident by the results of DSC analysis for binder I, which had a very small content of LMW crystalline fractions but still showed poor elongation properties at low temperature.

In the glassy state, amorphous components will act as rigid, stiff, and brittle molecular fractions and may cause the binder to exhibit poor extensibility and high stiffness. Results of DMA showed that asphalt binders characterized by high stiffness and poor extensibility at low temperatures have a higher T_g than that of low stiffness binders. As shown in Table 15, the glass transition temperatures for asphalt binders B4-PAV and B5-PAV (7.4 and 8.3°C, respectively) is higher than that of low stiffness asphalt binder D (3.5°C). The glass transition temperatures of binders B4 and B5, both as original and RTFO samples, were also higher than those of binder B3 for the same aging state.

Table 15
Glass transition (DMA) and the content of crystallizable species (DSC) of asphalt binders

Asphalt Binder	Glass Transition Tg (˚C)	Crystallizable Species Below 25°C (%)*	Crystallizable Species Above 25˚C (%)*
B3 original	-4.5	Not detected	0.18
B3 RTFO	-3.3	Not detected	0.41
B3 PAV	3.5	Not detected	0.37
B4 original	-7.5^	0.48	0.12
B4 RTFO	0.2	0.41	0.33
B4 PAV	7.4	0.86	Not detected
B5 original	5.0	0.03	0.12
B5 PAV	8.3	Not detected	0.10

- As a percentage of maltene fractions; ^ determined from DSC

FTIR Studies

FTIR Identification of THF Insoluble Species Captured on PTFE Filters. This work concentrated on detecting using FTIR what functional groups are not passing the PTFE filters used for GPC analysis (percentage insoluble in THF). The PTFE holder was careful cut and the filter papers spectra was recorded using a clean filter paper as background. An original SBS or SEBS (Figure 15) or aged polymer will have distinct peaks in FTIR spectra at wavelengths 1600 cm^{-1} and 966-969 cm^{-1} . None of these peaks were seen on filter papers for the samples examined in our project (Figure 16). These lead us to consider that the percent of insoluble polymeric species is insignificant compare to the percent of asphaltenes insoluble in THF and to apply composition corrections based upon weights of insolubles accordingly.

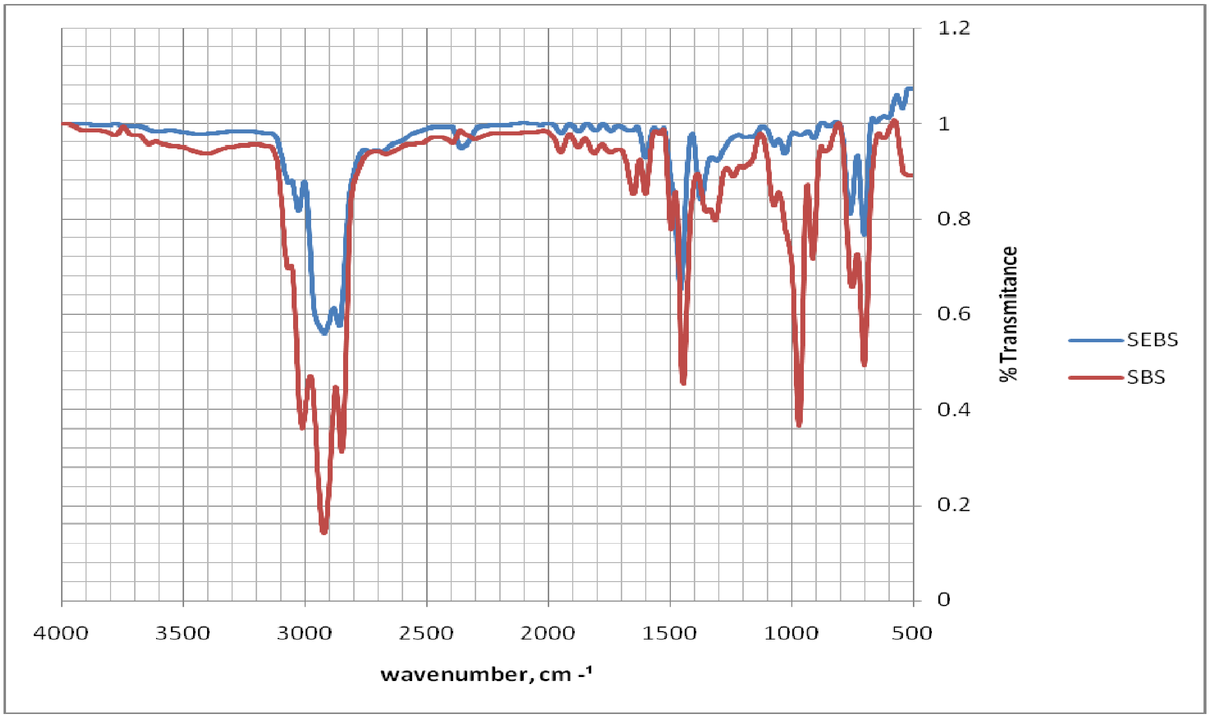

Figure 15
Original SEBS and SBS FTIR spectra

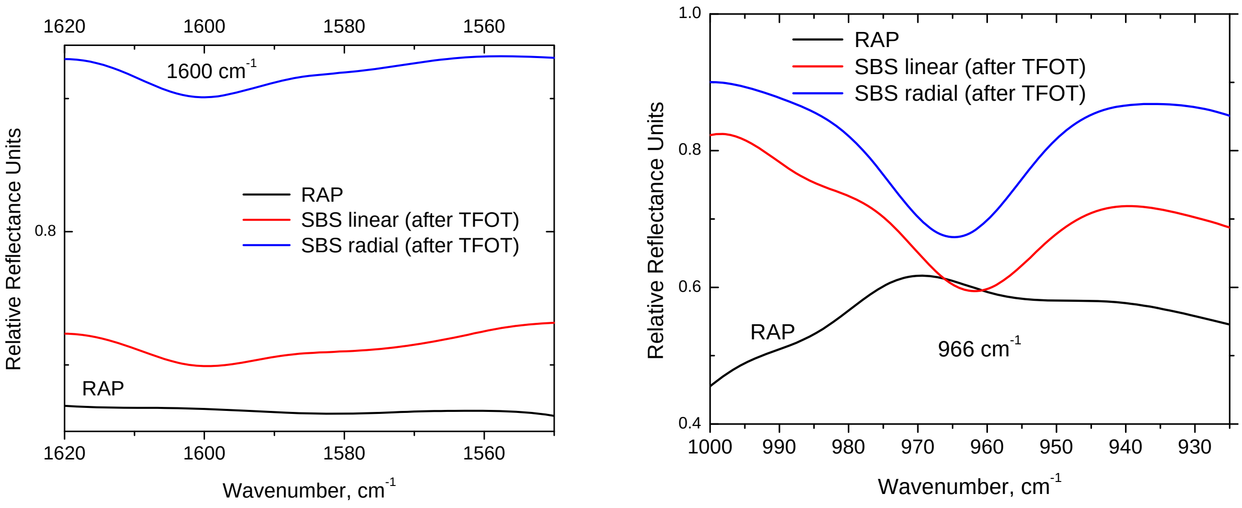

Figure 16
Example details FTIR spectra on filter paper

Asphalt Fractionation

Separation of Asphalt Components by Fractionation. In an effort to isolate samples of the asphalt components based upon their molecular weight differences, samples of asphalt were fractionated. The higher molecular weight components were considered less soluble in methanol toluene mixtures; the lowest concentration of methanol in the mixture should lead to the precipitation of the highest molecular weight component. To precipitate fractions of asphaltic material, methanol was added to toluene solutions. The following samples of asphalt binders were chosen for fractionation:

a. PG 64-22, refinery A, original, RTFO, and PAV
b. PG 70-22, refinery A, linear SBS, and low asphaltenes content
c. PG 76-22, refinery B, linear SBS, and higher asphaltenes content
d. PG 76-22, refinery D, radial SBS additive
e. radial SBS (note: linear SBS was received after the precipitation study was completed; it will be part of future work)

Asphalt binder solutions (10 wt%) in toluene were prepared (3% concentration solution for SBS). The solutions were diluted sequentially with aliquots of methanol to produce the solvent ratio desired. After the solution containing the resultant precipitate stood for 48 hours, the solution was decanted. The solvent in the wet residue was evaporated in the hood, and the residue was weighed and analyzed using both GPC and FTIR. The decanted solution was mixed each time with an appropriate volume of methanol to achieve the next ratio of toluene: methanol as presented in Table 16:

Table 16
Solvent ratios used and the fraction labels for asphalt fractionation

Ratio Toluene/ CH_3OH, mL/mL	100/0	80/20	70/30	60/40	50/50	40/60	30/70	20/80	0/100
Fraction A 64-22 original	zero	zero	F1	F2	F3	F4	F5	F6	F7
Fraction A 64-22 RTFO	zero	zero	zero	zero	zero	F1	F2	F3	F4
Fraction A 64-22 PAV	zero	zero	zero	zero	zero	F1	F2	F3	F4
Fractions A 70-22	zero	zero	F1	F2	F3	zero	zero	F6	F7
Fraction B 76-22	zero	zero	F1	F2	F3	F4	F5	F6	F7
Fraction D 76-22	zero	zero	F1	F2	F3	F4	zero	F6	F7
SBS	F1	F2	F3	F4	F5	F6	F7	F8	F9

A comparison with GPC data of the same material before fractionation was made and the findings are presented in Table 17 (all data have 0.1% – 0.2% error for region 1000-19K and 1-2% for region 19-0.2K). Sometimes the same fraction was hard to remove from the flask. In these cases, the fraction was labeled F*:

Table 17
Comparative GPC results from different asphalt binders and their fractions

GPC Run No.	Samples	VHMw 1000-300K	HMw 300-45K	MMW 45-19K	SUM 1000-19K	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K	Total
	A64-22original							
291	before fraction	0.0%	0.0%	0.0%	0.0%	14%	86%	100%
380	F1	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
381	F2	0.0%	0.0%	0.0%	0.0%	0%	0%	1%
382	F3	0.0%	0.0%	0.0%	0.0%	0%	0%	1%
383	F4	0.0%	0.0%	0.0%	0.0%	2%	1%	2%
384	F5	0.0%	0.0%	0.0%	0.0%	0%	2%	3%
385	F6	0.0%	0.0%	0.0%	0.0%	12%	80%	92%
386	F7	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
	Total	0.0%	0.0%	0.0%	0.0%	15%	84%	99%
	A 64-22 RTFO							
50	before fract.	0.0%	0.0%	0.0%	0.0%	20%	80%	100%
253	F1	0.0%	0.0%	0.1%	0.1%	1%	1%	2%
294	F2	0.0%	0.0%	0.0%	0.0%	1%	1%	2%
295	F3	0.0%	0.0%	0.0%	0.0%	6%	17%	23%
296	F4	0.0%	0.0%	0.0%	0.0%	12%	61%	73%
	Total	0.0%	0.0%	0.1%	0.1%	20%	80%	100%
	A 64-22 PAV							
53	PAV before fract.	0.0%	0.0%	0.0%	0.0%	23%	77%	100%
252	F1	0.0%	0.0%	0.1%	0.1%	1%	0%	1%
297	F2	0.0%	0.0%	0.1%	0.1%	2%	2%	5%
298	F3	0.0%	0.0%	0.0%	0.0%	4%	16%	20%
299	F4	0.0%	0.0%	0.0%	0.0%	16%	57%	73%
	Total	0.0%	0.0%	0.2%	0.2%	23%	76%	99%
	A 70-22							

288	before fract.	0.2%	0.6%	0.5%	1.3%	15%	84%	100%
374	F1	0.0%	0.2%	0.1%	0.3%	0%	1%	2%
375	F2	0.0%	0.0%	0.0%	0.1%	0%	0%	0%
376	F3	0.0%	0.2%	0.2%	0.4%	1%	1%	3%
378	F6	0.0%	0.0%	0.0%	0.0%	0%	5%	5%
379	F7	0.0%	0.1%	0.7%	0.8%	16%	74%	90%
	Total	0.0%	0.4%	1.1%	1.5%	18%	81%	101%
	B 76-22							
287	before fract.	0.2%	2.4%	1.7%	4.3%	22%	74%	100%
387	F1	0.0%	0.1%	0.1%	0.2%	0%	1%	1%
388	F2	0.0%	0.2%	0.2%	0.4%	1%	1%	2%
389	F3	0.0%	0.1%	0.1%	0.2%	1%	1%	2%
390	F4	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
391	F6	0.1%	1.4%	1.4%	3.0%	16%	61%	80%
392	F7	0.0%	0.0%	0.0%	0.1%	0%	0%	0%
393	F7*	0.0%	0.2%	0.2%	0.4%	3%	12%	15%
	Total	0.2%	2.1%	2.1%	4.4%	21%	75%	101%
	SBS							
112	before fract.	34.2%	52.1%	8.7%	95.0%	2%	3%	100%
335	F1	2.2%	2.3%	0.0%	4.6%	0%	0%	5%
336	F2	0.2%	0.8%	0.3%	1.3%	0%	0%	2%
337	F3	0.1%	1.0%	0.4%	1.6%	0%	0%	2%
338	F4	0.5%	0.8%	0.2%	1.5%	0%	0%	2%
339	F5	2.2%	11.3%	3.4%	16.9%	1%	0%	18%
341	F5*	0.8%	1.3%	0.7%	2.9%	0%	0%	3%
342	F5**	0.7%	0.8%	0.2%	1.7%	0%	0%	2%
340	F6	8.9%	51.0%	4.3%	64.2%	0%	0%	65%
344	F7	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
345	F8	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
343	F9	0.0%	0.0%	0.2%	0.2%	0%	0%	0%
	Total	15.7%	69.3%	9.6%	94.5%	1%	1%	97%
	D 76-22							
289	before fract.	0.7%	0.8%	0.6%	2.1%	14%	84%	100%
309	F1	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
310	F2	0.0%	0.0%	0.0%	0.0%	0%	0%	0%
229	F3	0.0%	0.3%	0.4%	0.7%	3%	1%	5%
230	F4	0.0%	0.0%	0.0%	0.1%	0%	0%	1%
231	F6	0.1%	0.4%	0.2%	0.8%	2%	9%	12%
232	F7	0.0%	0.3%	0.5%	0.7%	10%	74%	85%
	Total	0.1%	1.0%	1.2%	2.2%	15%	84%	102%

The method needs to be developed further, and more work should be done before reaching a final conclusion. Up to now researchers learned that a PG 64-22 asphalt binder can be identified as original or aged using the GPC method. An aged material will show an unusual distribution and a tendency to form asphaltenes-aggregates, which will be seen in GPC chromatogram in medium molecular weight region in a percentage of 0.1-0.4.

Applications of GPC Separation Technique

Analysis of Federal Highway Administration Samples. The following samples were analyzed using the GPC method. The results (Table 18) confirm a successful application of the GPC test.

Table 18
GPC results for FHWA samples

GPC		HMw	Asphaltenes	Maltenes	Total
Run		1000-19K	19-3.5K%	3.5-0.2K%	
No					
9	air blown original	0.2%	22%	78%	100%
29	after RTFO	0.3%	24%	76%	100%
28	after PAV	0.4%	25%	74%	100%
10	PG 76-22 SBS-linear original	4.8%	15%	80%	100%
11	after RTFO	4.0%	18%	78%	100%
34	after PAV	2.4%	19%	78%	100%
30	PG 70-22 original	1.1%	16%	83%	100%
21	after RTFO	0.3%	18%	81%	100%
32	after PAV	0.5%	21%	78%	100%
33	PG 64-40 with SBS, original	4.0%	13%	83%	100%
27	after RTFO	3.6%	15%	82%	100%
35	after PAV	3.5%	17%	80%	100%

Samples from Suspected Bleeding on BTR Airport Runway. In order to determine if asphalt bleeding occurred or if the oil layer was just an accidental spill, GPC chromatograms of samples from the surface with suspected bleeding (sample a) were compared with those of asphalt binder extracted from the core (sample b). The GPC results showed that both samples were perfectly identical; the curves are superimposable (Figure 17). The wet area must have stemmed from an accidental spill. The presence of area "asphaltenes1" shows that both asphalt binders were subjected to a mixing process that induced aging (comparable to RTFO samples). An un-oxidized binder does not have asphaltenes 1 region, around 19K (as was learned from separation by fractionation tests).

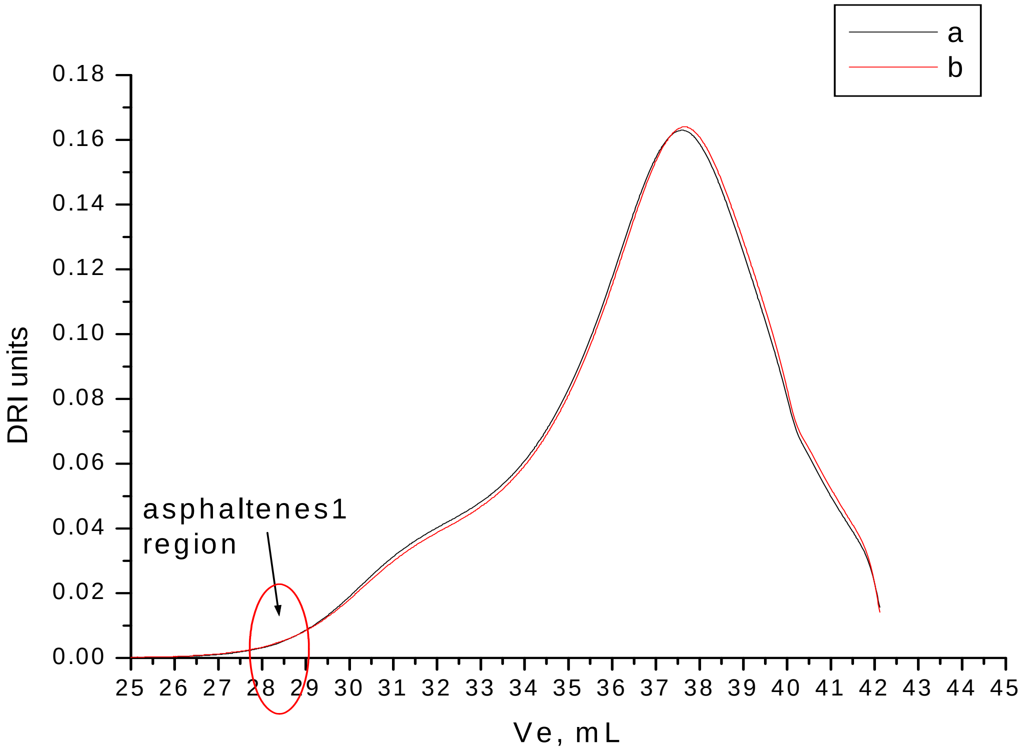

Figure 17
Molecular weight distribution of airport samples from GPC

CONCLUSIONS

This research demonstrated the application of GPC as an analytical tool to ascertain the amounts of polymer modifiers in polymer modified asphalt cements, which are soluble in eluting GPC solvents. The technique was applied to 29 samples from four refineries supplying asphalt mixes to Louisiana. The addition of RAP during the mixing process increases the asphaltene content with a corresponding decrease in the maltenes content. An assessment of the extent of oxidative aging of modified asphalt binders during the paving process illustrated minimal changes. Field aging of mixes containing RAP is slower than that predicted by RTFO laboratory aging, suggesting that the addition of 20 wt% RAP is beneficial to oxidative stabilization.

To meet the requirements for a PG 70-22, the researchers observed that 1% up to 2% polymer was added. To achieve PG 76-22, a minimum of 2 wt% polymer was observed. The GPC test method can identify the type of polymer used as well as the percentages of polymer and asphaltenes present.

The content of crystallizable species of selected asphalt binders determined by DSC is presented together with the glass transition temperature more accurately determined by DMA. A method for quantification of insoluble crumb rubber modifier present in crumb rubber modified binders was developed. The application of the technique to forensic studies of problem issues including high voids content and bleeding was demonstrated.

RECOMMENDATIONS

The GPC test should be implemented for all asphalt binders supplied to LADOTD. This equipment will provide positive chemical identification of polymer additives and a footprint chemical analysis of materials from each source. More research can be done to develop probable relationships of GPC data to physical properties.

ACRONYMS, ABBREVIATIONS, & SYMBOLS

µL	micro liter
Å	angstrom
AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
CR	crumb rubber
CRM	crumb rubber modified
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
DRI	differential refractive index
DSR	dynamic shear modulus
E*	dynamic complex modulus
FHWA	Federal Highway Administration
FTIR	Fourier transform infrared
G	gram
G*	complex shearing modulus
GPC	gel permeation chromatography
HMA	hot mix asphalt
HMw	high molecular weight
in vacuo	in a vacuum
Jnr	non-recovered compliance
kDa	kilo-Daltons
Kg	kilogram
LA	Louisiana
LADOTD	Louisiana Department of transportation and Development
LEQSF	Louisiana Education Quality Support Fund
log	logarithm
mg	milligram
mL	milliliters
mm	millimeters
µµ	micrometers
mm Hg	millimeters mercury column
MMw	medium molecular weight
mPa	millipascal
MSCR	multiple stress creep recovery
Mw	molecular weight

PAV	pressure aging vessel
PB	polybutadiene
PG	performance grading
pH	is a measure of the acidity or basicity of a solution
PMAC	polymer modified asphalt cement
PS	polystyrene
PTFE	polytetrafluoroethylene
RAP	Recycled Asphalt Pavement
rpm	rotations per minute
RTFO	rolling thin film oven
SBR	styrene-butadiene rubber
SBS	styrene-butadiene-styrene tri-block co-polymer
SEBS	styrene-ethylene-butadiene-styrene polymer
SUPERPAVE	SUperior PERforming Asphalt PAVEments
TFOT	thin film oven test
TGA	thermo-gravimetric analysis
Tg	glass transition temperature
THF	tetrahydrofuran
Ve	elution volume
VHMw	very high molecular weight
vide infra	see below
wt%	weight percentage
δ	phase angle

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APPENDIX A

Interpretation of GPC Data

For consistency, a baseline was drawn for each raw GPC data. To eliminate as much accumulation of error as possible, the data corresponding to a molecular weight higher than 1000 K and lower than 0.1 K were not saved. None of the samples showed species with a Mw higher than 1000 K and lower than 0.1 K that is the solvents region.

Data collection for the instrument was set up to a level of 60 slices. So, for an integrated area of 1, the sum of DRI values will be 60. Using an Excel program, each region was well delimitated using the calibration curve of elution volume, Ve, and the molecular weight of standards. For each region, the sum of DRI values was computed. By dividing these values by the total sum of the raw data, a percentage fraction weight was calculated. For graphical comparison, researchers used column 5 and for reporting percentage composition, column 6 (Table 20) was used.

Table 19
Excel worksheet used for GPC interpretation

Mw	Ve	GPC	Baseline	For graphs	% wt
Da	mL	Raw data	Col3-0.1645	Col4 *60/Total col3	Col5/Total col5
1	2	3	4	5	6
3408176	22	0.1645	0.0000	0.000000	0
3329668	22.02	0.1645	0.0000	0.000000	0
3291205	22.03	0.1645	0.0000	0.000000	0
3215821	22.05	0.1645	0.0000	0.000000	0
3142443	22.07	0.1645	0.0000	0.000000	0
3106486	22.08	0.1645	0.0000	0.000000	0
305364	24.32	0.1694	0.0049	0.001217	2.03E-05
303040	24.33	0.1694	0.0049	0.001217	2.03E-05
Total 1	***3266.50***	***23.45***	***0.25***	***0.06***	***0.00%***
298456	24.35	0.1694	0.0049	0.001217	2.03E-05
293958	24.37	0.1697	0.0052	0.001291	2.15E-05
101	42.1	0.3143	0.1498	0.037196	0.00062
100	42.12	0.3131	0.1486	0.036898	0.000615
Total	***38726.47***	***440.3549***	***241.6389***	***60.000000***	***1***

Fingerprint Data Base Using GPC Analysis

From GPC data, it can be seen that to meet the requirements for PG 70-22 a range from 1 to 2% polymeric additives was necessary. For a PG 76-22, a content higher than 2% polymer additives was shown by GPC. The PMAC extracted from plant mixtures (after drum mixing), and new pavement cores showed polymer contents higher than 2%. Data were correlated with rheological measurements

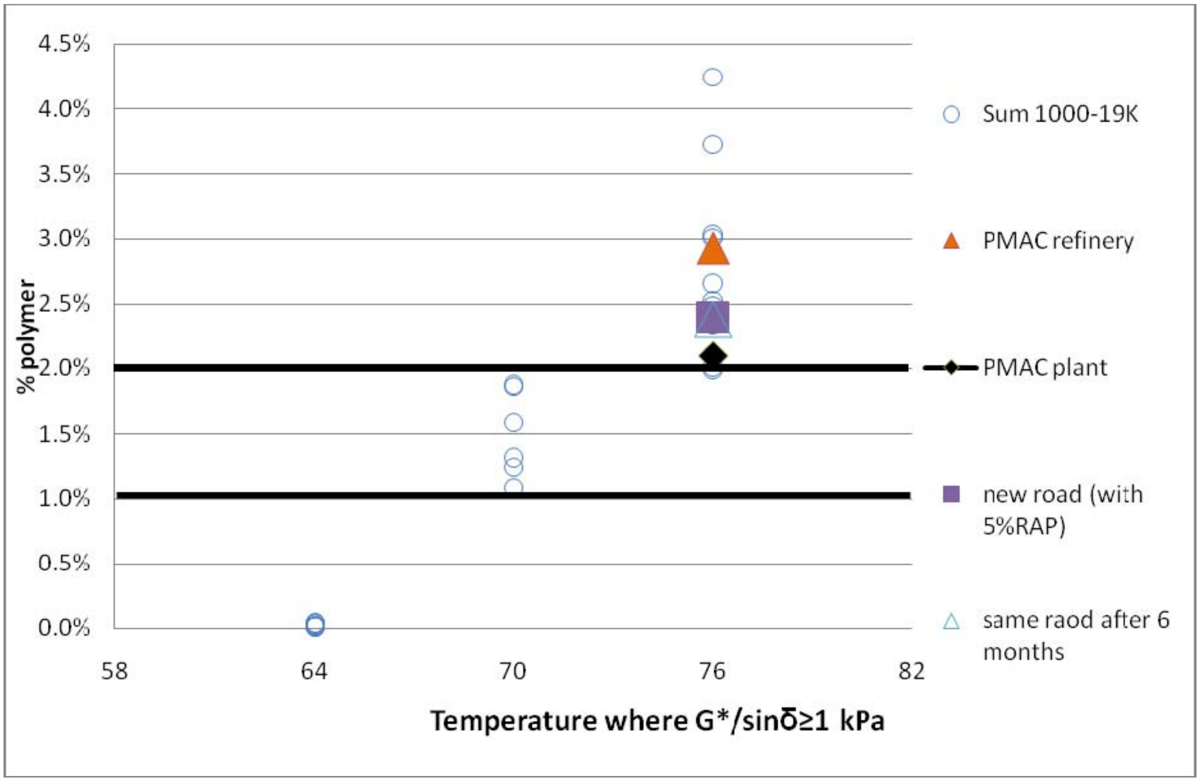

Figure 18
PG high temperature grading function of percentage polymer computed based on GPC analysis

Table 20
Analysis of crude oil sources *[23]*

Crude	**o API**	**Resin wt%**	**Asphaltene wt%**	**Asph./Resin**
Algeria, Hassi Messaoud	45	3.3	0.15	0.05
Brazil, Campos, Atabasca	19.7	21.55	2.8	0.13
Canada, Alberta	29	8.5	5.3	0.62
Canada, Atabasca	8.3	14	15	1.07
Canada, Cold Lake	10.2	25	13	0.52
France, Lagrave	43	7.5	4	0.53
Iraq, Kirkuk	36.1	15.5	1.3	0.08
Mexico, Isthmus	37.8	8.1	1.3	0.16
Mexico, Panucon	11.7	26	12.5	0.48
Mexico, Tecoaminocan	36.7	8.8	1.5	0.17
Russia, Balachany	31.7	6	0.5	0.08
Russia, Bibi-Eibat	32.1	9	0.3	0.03
Russia, Dossor	32.6	2.5	0	0
Russia, Kaluga	16.7	20	0.5	0.025
Russia, Surachany	35	4	0	0
USA, CA, Huntington Beach	26.2	19	4	0.21
USA, LA, Brookhaven	30.6	4.6	1.65	0.36
USA, LA, Rodessa	43.8	3.5	0	0
USA, MS, Baxterville	16	8.9	17.2	1.93
USA, OK, Davenport	46.3	1.3	0	0 0.00
USA, OK, Ok. City	38	5	0.1	0.02
USA, OK, Tonkawa	40.8	2.5	0.2	0.08
USA, PA	44.3	1.5	0	0
USA, TX, Hould	19.7	12	0.5	0.04
USA, TX, Mexia	36	5	1.3	0.26
Venezuela, Boscan	10.2	29.4	17.2	0.58