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16. Abstract

This research implemented a procedure for using gel permeation chromatography (GPC) as an analytical tool to define the percentage amounts of polymer modifiers, which are soluble in eluting GPC solvents, in polymer-modified asphalt cements. It also addressed quantification of both GPC solvent soluble and insoluble crumb rubber present in crumb rubber modified binders. Attention was also paid to using GPC for assessment of the extent of oxidative rolling thin-film oven (RTFO) and pressure aging vessel (PAV) aging of a series of asphalt binders as well as forensic analysis of pavement failures.

The project was sub-divided into two phases including (I) purchasing, installing and calibrating a GPC instrument at the DOTD Materials Laboratory and writing detailed procedures for conducting binder analysis to determine the percent polymer content in polymer modified binders and (II) developing an efficient extraction process capable of recovering binder from asphalt cement cores. Phase I included the GPC analysis of different polymers and binders, and a quantitative estimation of polymers, asphaltenes, and maltenes present in the analyzed binders. At DOTD, a large number of binders from various asphalt sources and polymer additives have been analyzed. Over 180 samples of PG 64-, PG 67-, PG 70-22m and PG 76-22m grades were subjected to GPC analysis and the polymer percentage was calculated and compiled. Phase II extended the development of a procedure to define the percent amounts GPC solvent insoluble crumb rubber present in CRM binders. It included a comparison between the extraction of soluble CRM species with a blend of toluene-ethanol (85:15 volumetric ratio) and bromopropane at room or moderate temperatures. Since similar results have been obtained, due to the fact that bromopropane is more expensive than toluene and ethanol, the toluene/ethanol mixture appears to be a better option, especially for large scale extractions. An AASHTO standard test method for the quantification of polymer content in polymer modified asphalt cements by GPC has been proposed.

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Implementation of GPC Characterization of Asphalt Binders at Louisiana Materials Laboratory

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October 2013

ABSTRACT

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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.
- Development of a simple GPC procedure for determining the composition of asphalt binders based upon the molecular size of the components.
- Installation of a robust GPC system in the DOTD Materials Laboratory.
- Establishment of a routine binder characterization method using GPC.
- Illustration of the forensic application of GPC to resolving mix problems encountered in the field.
- As part of the process for implementing the GPC device, a training session was conducted with LADOTD material lab technicians and chemists.
- Part of the implementation is to use the GPC device and method, in future LTRC/DOTD research projects on characterization of asphalts.
- Proposal of AASHTO standard test method for the quantification of polymer content in PMAC by High Performance Size Exclusion Chromatography (HPSEC), Appendix B.
- The GPC device is currently being used by LADOTD for Quality Control of the liquid asphalt binders received for testing by the Materials Lab. In addition, forensic evaluations using the GPC have been conducted on several LADOTD construction projects.
- LSU Chemistry department continues to support the use of the device by evaluating and comparing additional properties of the liquid binder to improve performance through a continuing research study, LTRC 12-3B.

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INTRODUCTION

Background and Significance of the Research

Asphalt is a mixture of wide variety of chemical compounds that include aliphatic hydrocarbons and highly fused aromatic ring systems. They are classified as asphaltenes (high molecular weight) and maltenes (low molecular weight). To improve the final properties of an asphalt binder, a high molecular weight polymer is added. In the case of polystyrene-b-polybutadiene-b-polystyrene, a block copolymer (SBS) and polystyrene-polybutadiene rubber (SBR) 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. Because there is a large difference between the molecular mass of polymer molecules and the mass of asphalt components (~ two orders of magnitude), the polymer can be easily visualized using a size exclusion analysis, such as GPC). The polymer and asphalt components of polymer modified asphalt cements can be separated completely using gel permeation chromatography *[1-4]*.

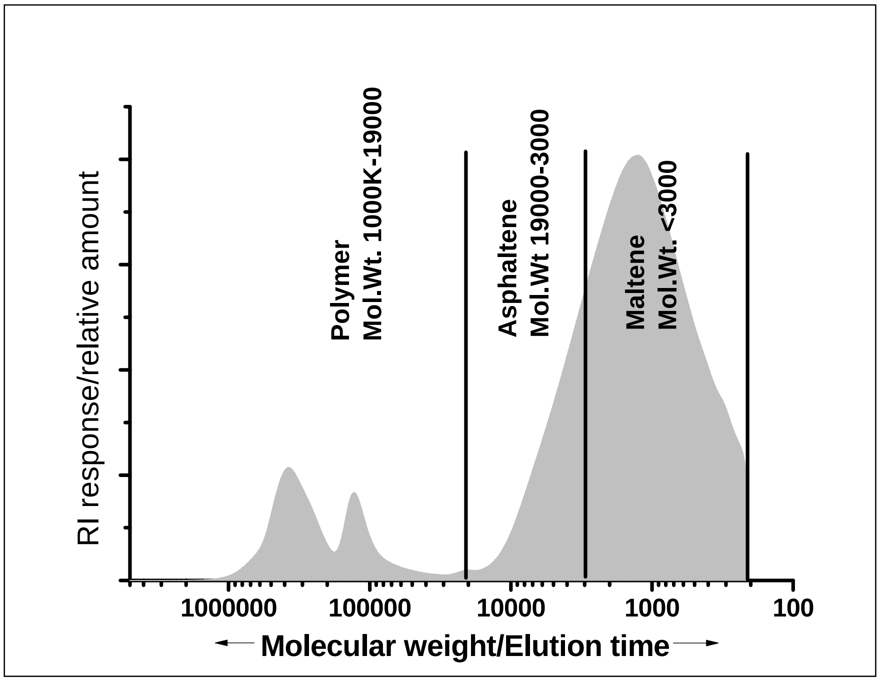


Figure 1
Molecular weight zones assigned in PMAC GPC chromatogram

Tetrahydrofuran (THF) solutions of binder samples are injected onto a set of porous columns and eluted with THF. The order of elution is related to the molecular weight (MW) of the component. High molecular weight species elute first, followed by molecules with ever-decreasing molecular weight. As shown in Figure 1, the SBS polymer with a molecular weight greater than 19,000 Daltons elutes first at the shortest time followed by the asphaltenes with molecular weights between 3000 and 19000 Daltons and finally the maltenes with molecular weights below 3000 Daltons. The area under the elution curve is directly proportional to the relative concentrations of each component so the analysis is quantitative. Changes due to asphalt aging, which leads to the formation of higher molecular weight asphaltenes due to aggregation as well as polymer degradation products, can be followed using the GPC method. It is of interest to apply GPC methodology to routine characterization of asphalt binders and to employ the technique in forensic analysis of paving problems. The project involved (1) quantitatively assessing the amount of the polymeric species in a polymer modified asphalt binder; (2) evaluating mixtures containing a crumb rubber modifier (CRM), which is practically insoluble in GPC solvents; and (3) analyzing asphalt emulsions.

OBJECTIVES AND SCOPE

This research was performed in order to implement a procedure for using gel permeation chromatography at the DOTD Materials Laboratory as an analytical tool to define the percentage amounts of polymer modifiers in polymer-modified asphalt cements. It also addressed the quantification of GPC solvent insoluble crumb rubber modifier present in CRM binders and analysis of asphalt emulsions. The GPC technique was also used for assessment of the extent of laboratory oxidative aging of FHWA reference asphalt binders, forensic analysis of pavement failures, and analysis of asphalt emulsions.

The project was sub-divided into two phases including (I) the purchase, installation and calibration of a GPC instrument at the DOTD Materials Laboratory and conducting tutorials regarding detailed procedures for conducting binder analysis to determine the percent polymer content in polymer modified binders, and (II) developing more efficient extraction processes capable of recovering asphalt from CRM asphalt cements. A collection containing over 200 GPC data has been obtained by analyzing binders and polymer additives from various asphalt sources and polymer additives.

METHODOLOGY

GPC is a method of separating molecules based on their size and shape in solution. The column used for separating the molecules (stationary phase) is packed with a porous bead- like crosslinked polymer network of styrene-divinylbenzene copolymers with closely controlled pores of variable sizes that can separate molecules in a particular molecular weight range *[5-7]*. Depending on the size and shape, solute molecules may be able to enter the pores of the stationary phase particles. Molecules larger than the pores will be totally excluded and will elute first. Very small molecules can enter every pore and permeate well into the stationary phase particles. These are retained most and hence appear last in the chromatogram. Intermediate size molecules elute at times depending on their comparative size. The size-separated molecules are detected and recorded according to their concentration. Through calibration, sizes are converted to molecular weights and various molecular weight parameters for the sample are calculated from the molecular weight-concentration data.

Description of Terms

GPC (Gel Permeation Chromatography): a chromatographic method of separation of molecules based on their size in a solution of a particular solvent). GPC is also known as size exclusion chromatography (SEC).

Differential Refractive Index detector (DRI): This detector measures the change in the refractive index of the solution (with respect to the solvent) that is eluting from the columns. The DRI is directly related to the concentration of the component in the solution passing through the detector.

Retention time: The time it takes for a particular component in the solution to pass from the injector through the columns to the detector.

Chromatogram: A plot of elution volume vs. refractive index detector response, or a plot of molecular weight or log molecular weight vs. refractive index detector response. In the latter case, the retention volumes are converted into molecular weight using a calibration curve prepared using narrow molecular weight polystyrene standards.

SBS: A polystyrene-b-polybutadiene-b-polystyrene block copolymer employed as a polymer additive.

Asphaltenes : The fraction of asphalt that is insoluble in n-heptane and is considered as a complex mixture of large aromatic molecules existing as aggregates in asphalt. Asphaltenes are high molecular weight and most polar fraction of asphalt.

Maltenes: Maltenes constitute the fraction of asphalt that is soluble in n-alkane solvent such as pentane and heptane. It contains low molecular weight resins, aromatic hydrocarbons, and cyclic unsaturated and saturated hydrocarbons**.**

Instrumentation & Presentation of the GPC Instrument

The basic parts of a GPC system are:

1) A solvent reservoir to hold sufficient amount of solvent.
2) A pumping system to deliver the solvent at a constant flow rate.
3) A sample injector to inject a specific quantity of sample solution as sharply defined zone into the solvent stream.
4) Columns of required pore sizes, selected in such a way that the molecular weight range of the polymer falls within the separating range of these columns. At the higher end of this range is the exclusion limit, at which all molecular weight beyond the working range are eluted simultaneously, and at the lower end is the permeation limit, at which molecules of molecular weight below the working range elute together.
5) Detectors to provide an index of concentration of the molecules in the stream emerging from the columns. The detectors used in this study are:
    1. A DRI detector (which provides a signal proportional to the difference in refractive index between the solvent and the solution stream coming from the columns). The DRI response (RI) is directly proportional to the concentration of the components present in the mixture.
    2. A UV-detector, which is applicable when solute adsorbs the incident wavelength
    while the solvent does not.
6) A data processing system that generates plots of eluting species concentration as a function of elution time. The data processing system calculates the various molecular weight averages based upon a calibration table developed by injecting samples with known molecular weights.

In the present work, the EcoSEC high performance GPC system (HLC-8320GPC) Figure 2, was employed. The instrument has been purchased for the DOTD Materials Laboratory from the Tosoh Corporation (Tosoh Bioscience LLC, King of Prussia, PA), which won the bid and all the data presented in this report have been acquired with it. This system compactly assembles an auto-injector, auto-sampler, high pressure pump with a degasser, and an oven containing the columns listed below, along with DRI and UV detectors. The actual data was collected and analyzed using an EcoSEC-Workstation. Refinement of data analysis in order to quantify the asphalt species (i.e., the content of polymer, asphaltenes, and maltenes) has been made using the Origin 6-8.5 software.

Figure 2
Tosoh EcoSEC high performance GPC system (HLC-8320GPC) from LA DOTD Materials Laboratory

Materials and Reagents

Reagents

1. Tetrahydrofuran (THF) HPLC grade - Solvent
2. Butylated hydroxytoluene (BHT) - Peroxide inhibitor

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.

Materials

1. Glass Scintillation vials (20 mL) with cone screw caps, Wheaton* Glass 20mL scintillation Vials with Poly-seal Cone Cap Liner, Wheaton Science Products Inc. No. 986586 or equivalent

2. Glass Burette 25 mL
3. 3mL Disposable Syringes: AirTite^{TM} Norm-Ject^{TM} with Luer-Lok^{TM} fitting, Air Tite Products Co No. AL3, (Fisher Scientific catalog number: 14-817-27) or equivalent.
4. Needles- Gauge: 18; O.D.: 1.24 mm; Length: 38 mm, BD Precision Glide* BD Medical No.:305196 (Fisher Scientific catalog number 14-826-5D) or equivalent.
5. Pipette bulb 2mL (Fisher Scientific No**:** 15-000-506) or equivalent.
6. Syringe Filters with Luer-Lok^{TM} Inlet, PTFE; Diameter: 13mm; Porosity: 0.45um **(**Restek Catalog No: 06-802-785, Color: orange Fisher Scientific catalog No 06-802-785) or equivalent.
7. 2 mL Autosampler vials; Clear Glass with Write-on Spot; Screw-top without cap, (Krackeler Scientific Agilent No.:5182-0715 (Fisher Scientific catalog No. HP 51820715N) or equivalent.
8. Screw Caps for the auto sampler with Septa, (Krackeler Scientific Agilent No. 51820717N, Fisher Scientific catalog No. HP 51820717N)) or equivalent.
9. Mobile phase Guard column Guard SuperHz-2 Tosoh or equivalent with the following separate columns:
    a. TSK gel, Super Hz 4000, 6.0 mm ID x 15 cm, pore size 200Ǻ, polystyrene MW range exclusion 4×10^5 (1 column)
    b. TSK gel, Super Hz 3000, 6.0 mm ID x 15 cm, pore size 75Ǻ, polystyrene MW range exclusion 6×10^4 (2 columns)
    c. TSK gel, Super Hz 2500, 6.0 mm ID x 15 cm, pore size 30Ǻ, polystyrene MW range exclusion 2×10^4 (1 column)

Preparation of Standard Solutions

Calibration standards, PStQuick series (B, E, and F) were used to calibrate the GPC columns. Each of these standards is a mixture of narrow molecular weight polystyrenes with different molecular weights. Tosoh PStQuick series (B, E, and F) which come pre-weighed in glass vials. Each vial contains mixture of different narrow molecular weight standards of polystyrenes. Add 1 mL of THF in these vials, close the screw caps, and allow to stand overnight without shaking. Prior to analysis the vial should be shaken gently. These standards provide a wide range of molecular weight standards, which extends from very high molecular weight to very low molecular weight. It is ideal for the analysis of a mixture asphalt (low molecular weight) and polymer (high molecular weight). The following standard mixtures were employed:

3.1 PStQuick B (MW= 5480000, 706000, 96400, 10200, 1000)
3.2 PStQuick E (MW= 355000, 37900, 5970, 1000)
3.3 PstQuick F (MW= 190000, 18100, 2500, 500**)**

Sample Preparation

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.

Preparation of 1% solution: Weigh ~100mg (± 0.5 mg) of asphalt into a 10mL volumetric flask using an analytical balance. Add THF to 10 mL and close the flask tightly. After mixing it gently, keep the flask overnight for the complete dissolution. Prior to filtration, mix the contents again. Alternatively, ~100mg (± 0.5 mg) of asphalt can be weighed into a 20 mL scintillation vial and exactly 10 mL THF can be added to the vial using a burette. Seal with a screw cap, mix, and keep overnight for the complete dissolution. Prior to filtration, mix the contents again.

Preparation of 0.25% solution: Using an analytical balance, weigh ~25mg (± 0.5 mg) of asphalt and prepare a solution as described above.

Solution filtration: A 5 mL syringe, 0.45um PTFE filter and disposable glass pipette with rubber bulb are required for this. First remove the plunger of the syringe attached to a 0.45um PTFE filter via a Luer-Lok^{TM}. Carefully add 2.3 mL of asphalt solution into the syringe using a disposable pipette. Insert the plunger back into the open syringe, while carefully inserting the filter outlet into an auto sampler vial. Push the plunger slowly so that filtered solution collects in the vial. Cap and label the vial.

GPC Procedure

In the TOSOH GPC system (HLC-8320GPC), the operation of the instrument and setting of parameters are performed in the instrument control screen of the Acquisition control program. To begin analysis, press the power button at the top of the acquisition control program screen and click on warm up screen. Click the instrument parameter from the operating menu and select the desired parameters for analysis. The following settings were employed: solvent flow rate, 0.35 mL/min; reference flow ratio, equal; column and pump oven temperature, 40°C. Set the RI detector balance value (mV) to 30.000 and response (sec) to 0.5. Set the UV detector wavelength (nm) to 254 (if needed) and Balance value (nm) to 30.000, and response (sec) to 0.5. Click the warm up tab to bring the warm up screen. Allow 2 hours for the instrument to complete the warming up process.

Set the solvent (THF, tetrahydrofuran) flow rate to 0.35 mL/min, reference flow ratio to equal, column and pump oven temperature to 40°C. Set the RI detector Balance value (mV) to 30.000 and response (sec) to 0.5. Set the UV detector wavelength (nm) to 254 (if needed) and Balance value (nm) to 30.000, and response (sec) to 0.5. Click the warm up tab to bring the warm up screen. Give time for complete warming up process and for a stable RI base line. All data collected in the present report have been acquired using the best combination of columns for GPC analysis at room temperature, viz., the four column set described above (Materials section, #9). Using sample concentrations of 0.25% or 1.00% and eluting at 0.35 mL/min (if not stated otherwise), the total time for a sample analysis was less than 60 minutes.

Calibration

First, calibrate the instrument using freshly prepared calibration standard solutions (PStquick B, E & F or equivalent) in the given vials (2 mL), as explained in the previous section. Load the auto sampler by pressing the rack eject/insert key in the control section of the instrument. Place the solution vials on to the auto sampler. Remount the sample rack on the instrument by pressing rack eject/insert key. Click on the sample queue screen on the acquisition control program; enter the sample queue name, name of the samples, and various settings for the solutions loaded in the auto sampler. Follow the quick reference manual for the instructions. For calibration standards, total time for analysis is 30 minutes, injection volume 10 µL, two repeat, 254 nm as UV wavelength. After entering these values, check the error and start analysis. Use the quick reference manual of High-performance GPC system HLC-8320GPC EcoSEC-WorkStation for creating method, calibration, analysis conditions, and saving of the data.

The chromatograms of the PST quick B, E and F are shown in Figures 3, 4 and 5. Open the analysis program and use the GPC software to do a base line correction, and peak edition to obtain a retention time for each peak. In the calibration method screen of the software, enter the retention values (peak maximum) and corresponding molecular weights of the standards in the three solutions in a table as instructed in the instrument software (shown in table 1). The combined calibration data is shown in Figure 6. The software will create a calibration curve of retention time vs. log molecular weight as shown in Figure 7. This will be used for the analysis of asphalt samples.

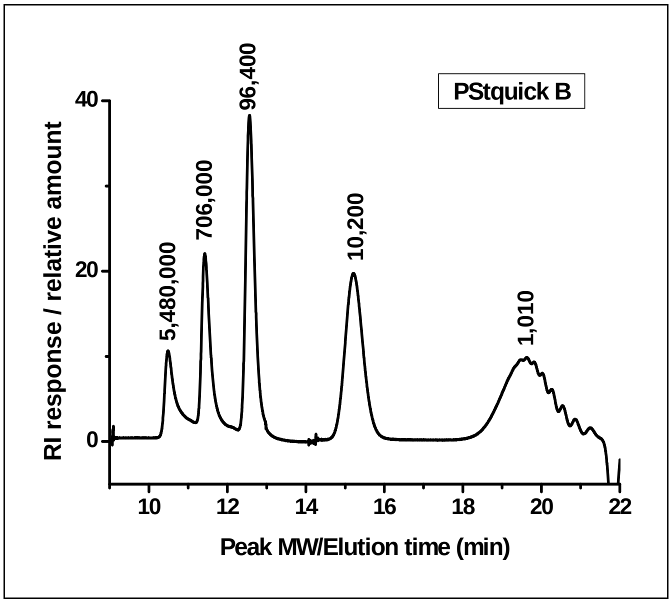


Figure 3

GPC chromatogram of PStQuick B in THF, 0.35ml/minute, 40°C

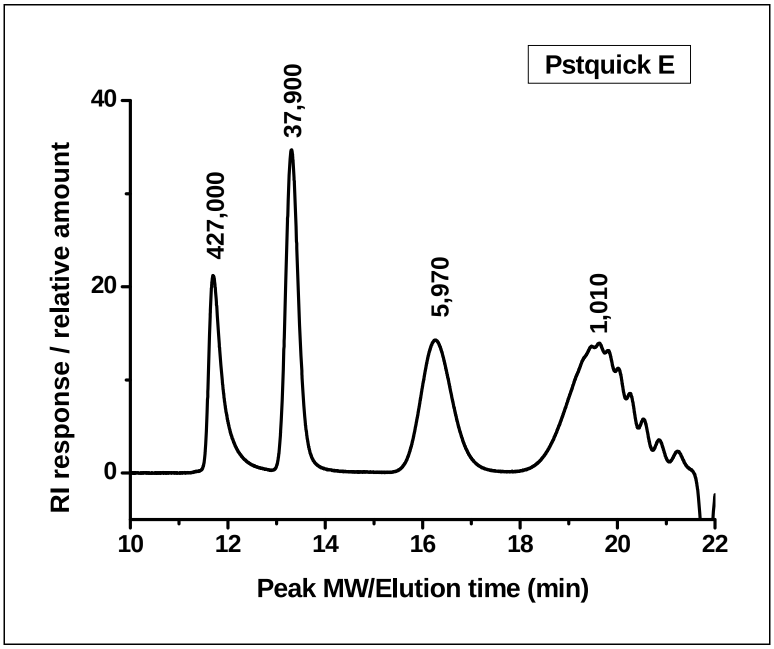


Figure 4

GPC chromatogram of PStQuick E in THF, 0.35ml/minute, 40°C

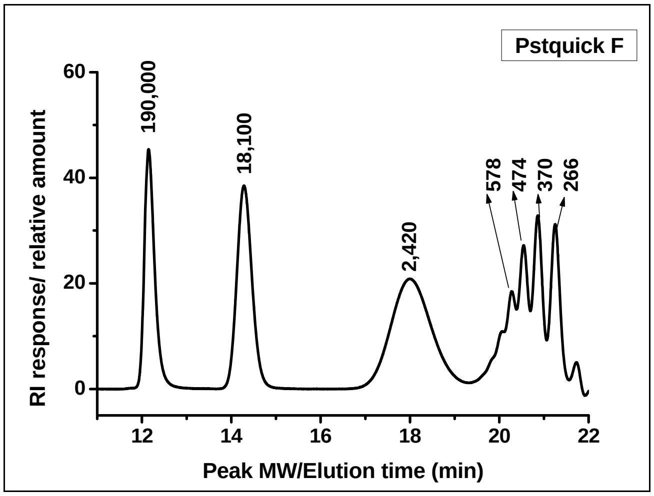


Figure 5

GPC chromatogram of PStQuick F in THF, 0.35ml/minute, 40°C

Table 1

Example of GPC calibration data obtained using Pstquick B, E, and F series

Retention time (min.)	**Molecular weight (Daltons)**	**Log molecular weight**
10.487	5480000	6.73878
11.427	706000	5.8488
11.695	427000	5.63043
12.147	190000	5.27875
12.565	96400	4.98408
13.308	37900	4.57864
14.282	18100	4.25768
15.215	10200	4.0086
16.262	5970	3.77597
17.995	2420	3.38382
19.623	1010	3.00432
19.637	1010	3.00432
20.278	578	2.76193
20.543	474	2.67578
20.863	370	2.5682
21.252	266	2.42488

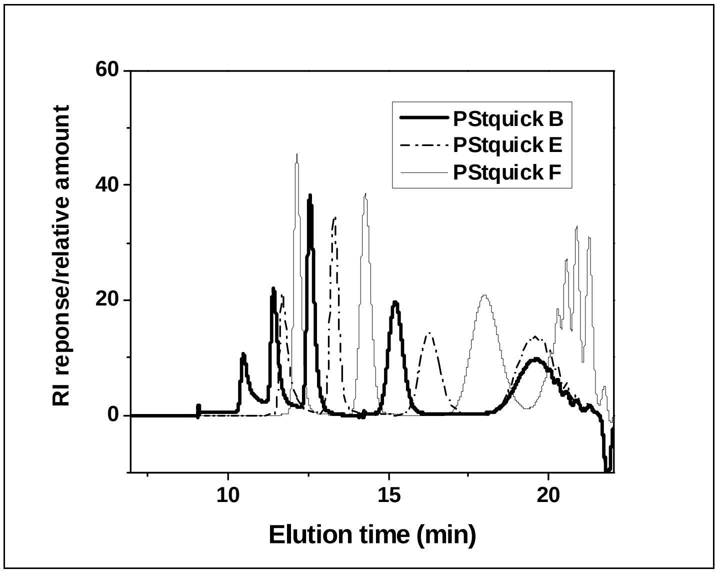


Figure 6
Combined chromatograms of polystyrene standards

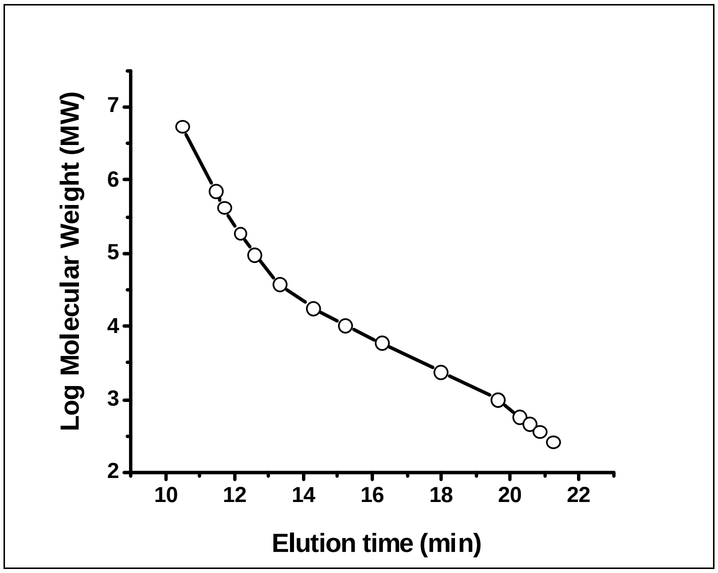
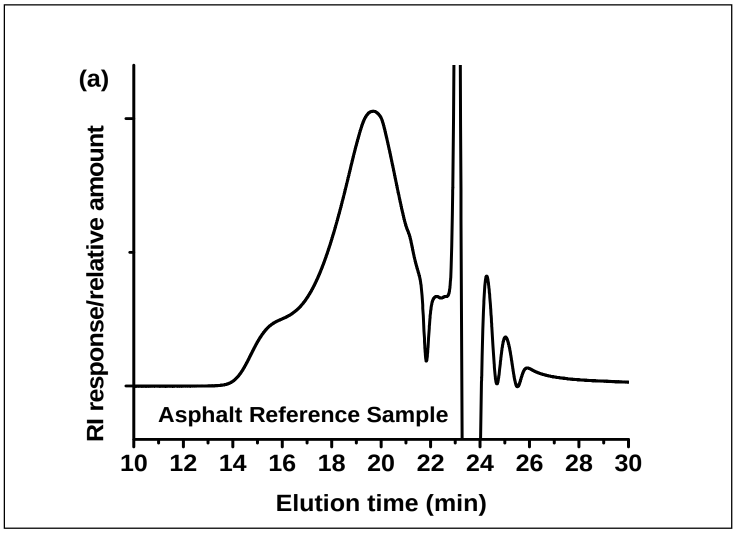


Figure 7
Calibration curve prepared from elution time of polystyrene standards

Instructions for Analysis of Asphalt and Related Samples

Prepare a solution as previously explained in an earlier section. Using 15 cm columns, a 0.25 wt%/volume solution gives good detector response, which has comparable magnitude to the PS standards. If 30 cm columns are used, the solution concentration should be raised to 1.0 wt %/volume. Filter the solution to 2 mL vials suitable for use in auto sampler. Load the samples and use the same settings as for the calibration except the time of analysis. For asphalt analysis, 30 minutes is satisfactory but 60 minutes assures that the column is completely flushed of all the components of asphalt. 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.

Typical chromatogram of the 1% solution of the reference asphalt (Company A) in the THF solvent is shown in Figure 8. This is an example of asphalt that has no polymer added to it. Figure 8(a) 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 8b.



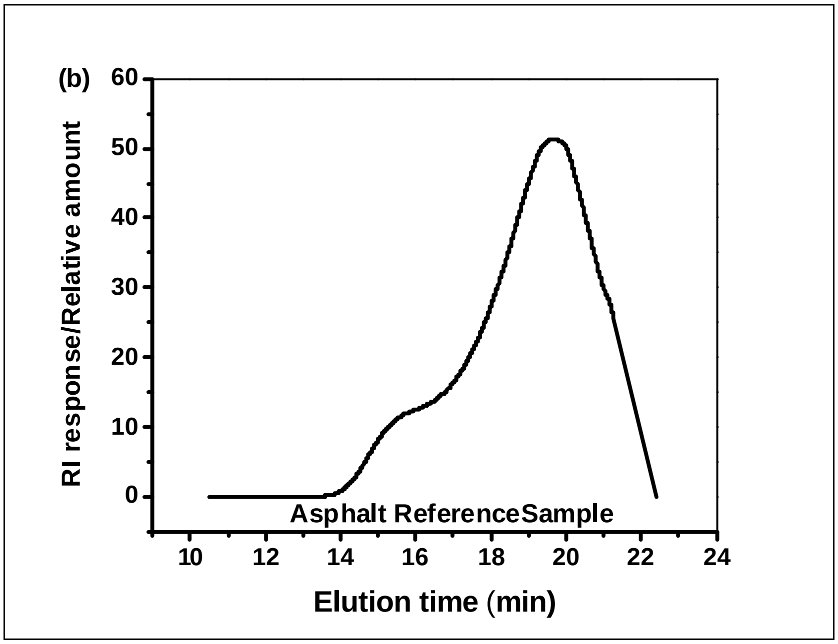
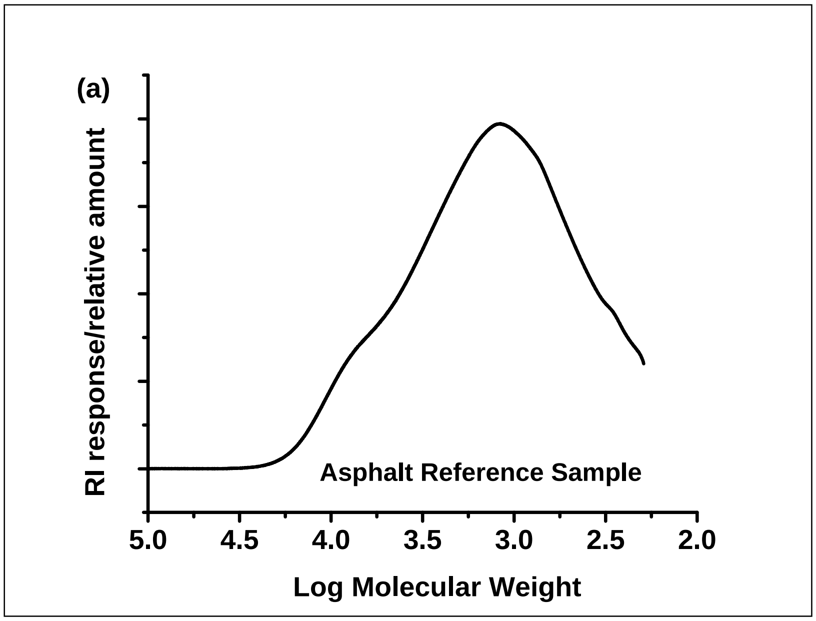


Figure 8

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

The retention times are then converted to log molecular weight as shown in Figure 9(a) and converted to molecular weights in Figure 9(b), respectively using the calibration curve obtained with polystyrene standards. Figure 9(b) shows that the typical asphalt components have molecular weights ranging from 19,000 to 200 Daltons (based on polystyrene molecular weights).



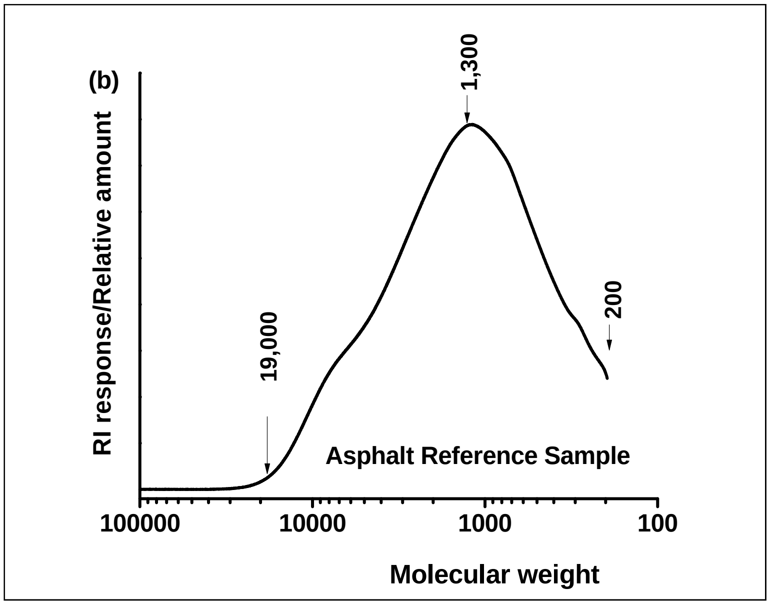


Figure 9

(a) Retention times in the chromatogram shown in Figure 8 are converted to log molecular weights and (b) molecular weight distribution curve made using calibration data obtained with polystyrene standards

GPC Analysis and Quantification of Polymer-Modified Asphalt into Polymers, Asphaltenes, and Maltenes

Typical polymer and asphalt chromatograms are shown in Figure 10. A clear separation of polymer from asphalt can be seen. The polymer, having a higher molecular weight compared to that of the asphalt, comes in the range of MW of 1,000,000 to 19,000 Daltons. This difference in molecular weight makes it easy to quantify the amount of polymer in a blend of polymer and asphalt or in PMAC materials.

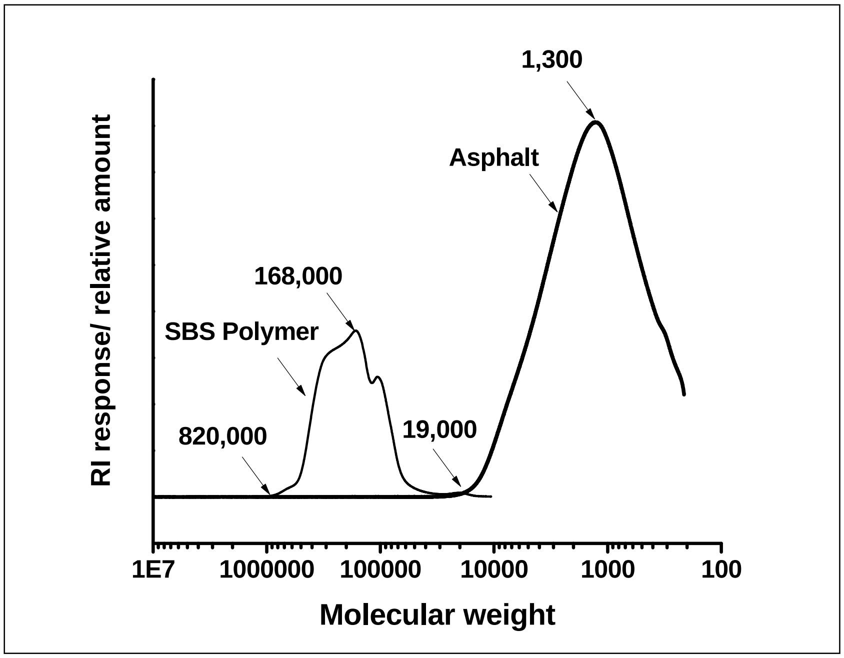


Figure 10
GPC Chromatograms of an asphalt and SBS polymer (Company A)

The area from 19,000 to the low molecular weight end can be considered as total asphalt present (viz., containing only asphaltenes and maltenes). There are no accurate standards available that gives the molecular weight distribution of asphaltenes and maltenes species, due to their molecular complexity nature and/or association. When considering GPC, the eluting molecules are separated according to their molecular size. The chemical composition of the asphalt can interfere with separation in GPC by intermolecular association, the association with solvent and interaction with column material. It is possible that some asphaltenes, considered to be the high molecular weight fraction of asphalt, can interact with the column filling material and might dissociate, coming out as a component of much lower molecular weight. Earlier studies of separating asphalt into asphaltenes and maltenes by extraction and GPC analysis of the fractions showed that the molecular weight of asphaltenes and maltenes can tail from one end to the other end of the chromatogram, with the major portions coming as high molecular weight and low molecular weight, respectively *[8-9]*. This may be due to the inefficiency of the GPC separation or of the extraction procedure used to separate them.

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) *[1,10,11*]. It is also reported that the LMS region can be correlated with physical properties and field performance of the asphalt analyzed *[12-14]*. 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 [*15*]. 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 three slices based on the molecular weight of the eluting species, and the calibration curve made using polystyrene standards *[16-18]*. The three fractions are polymers (molecular weight greater than 19,000), asphaltenes (molecular weight from 19,000 to 3,000), and maltenes (molecular weight less than 3000) as shown in Figure 1. Quantitative data can be obtained by determining the area under the curve as shown in Figure 1. For the quantitative estimation of the area was calculated using the Origin software (it can be also obtained from the instrument software). Analyzing a large number of asphalts and correlating these values with binder properties can give a better understanding in the selection/modification of asphalt with better performance.

Effect of Concentration of Sample in GPC Analysis

Using an RI detector, the detection limits will be controlled by the difference in the refractive index between the solute and the solvent. Associating components, such as asphaltenes can appear to have a larger molecular size in poor solvents, particularly at high solute concentrations. These issues are quite critical if the goal is to resolve the components of the asphalt binder. However, if the objective is to determine the polymer concentration relative in the binder, solute association is not critical.

Two possible solvents were examined, toluene and THF, in this work. The sensitivity of the detection was reduced when samples were eluted with toluene because the differential refractive index was too small. Further, the asphaltene components tended to tail badly indicating selective adsorption of the asphaltenes on the crosslinked polystyrene columns. Therefore, THF was used as the eluting solvent. Dissolution of asphalts in solvents tend to promote aggregation with time, which increases the apparent concentration of asphaltenes, so samples should be run on the same day they are prepared.

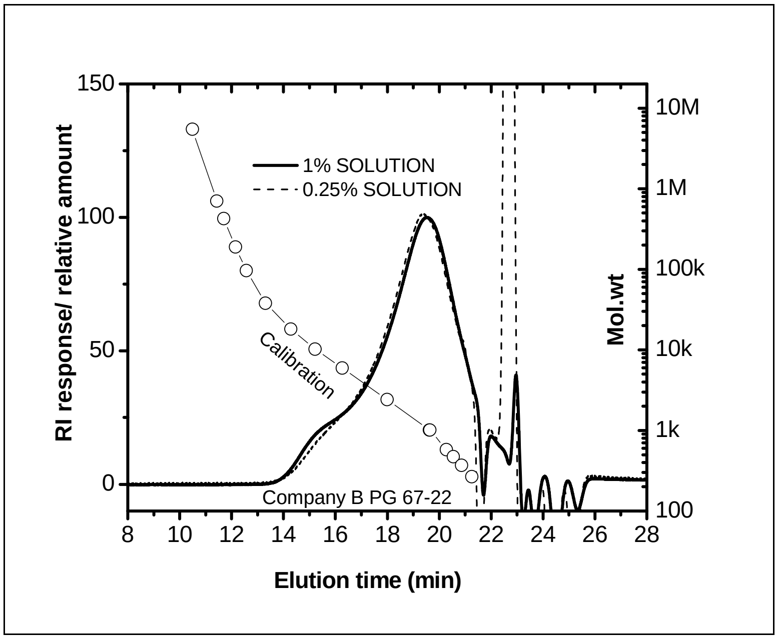
Experiments were conducted to check to see if the effect of concentration of THF solution used in GPC has any effect on the MWD of asphalt components elute at different times. An unmodified asphalt cement (AC) and a PMAC sourced from two different companies were used for this test . The two different concentrations used were 0.25% and 1%.

The influence of concentration on two sources of asphalt is shown in Table 2. In each case, the apparent polymer content increased at the lower concentration. At lower concentrations, the solution viscosity is minimized and the tendency for peak spreading is reduced. It is suggested that low concentration of 0.25% is better than 1%, as it introduces less amounts of samples in the column. In each case, the apparent polymer content increased at the lower concentration.

Table 2
Results of analysis of GPC solutions with two different asphalt concentrations

Sample	**Conc. (%)**	**1M-300K %**	**300-45K %**	**45-19K %**	**Total Polymer% >19K**	**Asphaltenes % 19K-3000**	**Maltenes % <3000**
Company B PG 67-22 AC	**1**	0	0	0.38	0.38	20.75	78.86
	0.25	0.12	0.13	0.43	0.68	19.69	79.63
Company C PG 70-22m PMAC	**1**	0.03	1.19	1.06	2.27	22.32	75.41
	0.25	0.20	1.34	0.99	2.53	20.80	76.66

Figure 11 presents the corresponding chromatograms (normalized to see the changes) of the two asphalts (AC and PMAC) injected at two different concentrations. It was observed that there is a slight effect of concentration on the high molecular weight portion of the curve. The 1% solution of AC and that of the PMAC showed a small hump toward a high molecular weight area, which may be due to the increasing association of asphaltenes species. At lower concentrations, the solution viscosity is minimized and the tendency for peak spreading is reduced. Overall, there is a small change in the percentages of polymers, asphaltenes, and maltenes.



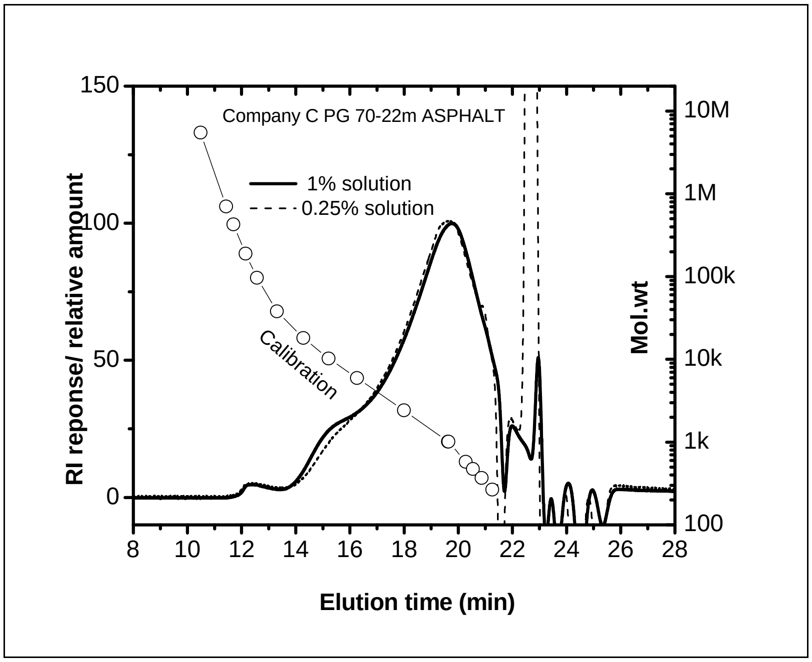


Figure 11

GPC traces of asphalt materials from Company B (top) and Company C (bottom) obtained at 1% and 0.25% sample concentrations in THF

GPC Analysis of Neat (AC) and Polymer Modified Asphalt (PMAC)

Unmodified or neat asphalt is sensitive to high and low temperatures when used in roads. During the summer, this asphalt softens, while during winter it becomes more rigid and tends to crack. These changes can cause rutting and deformation. To get a good performance, high molecular weight polymers are added, which make the asphalt more elastic over a larger temperature domain. The most common polymer modifier is the SBS polymer. The following is an actual example of GPC data acquired for base asphalt cement and for its blend with a polymer at high level (12wt%) for a better representation. Figure 12 shows the superimposed chromatograms of neat asphalt and PMAC. A clear peak of polymer away from the asphalt can be seen. Analysis (Table 3) found out that PMAC contains ~12% polymer.

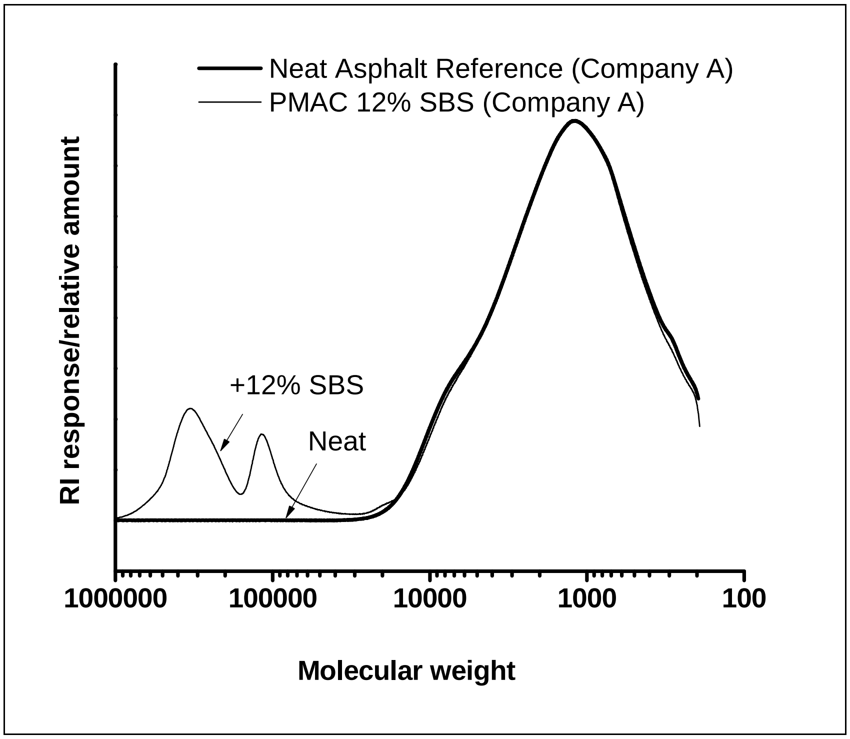


Figure 12

Superimposed GPC traces of neat asphalt and of its derived PMAC

Table 3
Results of GPC analysis of neat asphalt and of its derived PMAC

Sample	1000K - 300K %	300K – 45K %	45K-19K %	**Total polymer (%)**	**Asphaltene (%)**	**Maltene (%)**
PMAC Reference Company A	5.92	5.82	0.67	**12.41**	**16.81**	**70.77**
Asphalt Reference Company A	0	0	0.22	**0.22**	**19.44**	**80.34**

Procedure to Detect Percentage of Crumb Rubber in Asphalt Blends and in Paving Mixtures

First, a sample of crumb rubber (CRM) containing the additives and fillers from the rubber processing should be extracted in hot toluene in order to determine the amount of soluble rubber additives and have the additives removed. The procedure is as follows:

1. Weigh 1 to 10 grams of crumb rubber into a tarred beaker; record the sample weight as initial mass.
2. Add 50 mL of toluene preheated to 70º C.
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. Evaporate the toluene extracts to dryness using a rotary evaporator. An aliquot of the residue can be re-dissolved in THF as described above under the heading **sample preparation**.
7. If filter papers tend to clog, use as many filter papers as you need to collect the full quantity of insoluble crumb rubber.
8. Dry filter papers in vacuum oven for 3 hours at 80°C.
9. 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 insoluble material.
10. Compute the weight of the soluble from the difference in weight: initial mass – final mass.

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

Secondly, an unknown CRM (crumb rubber modified) asphalt modified asphalt liquid can be analyzed to determine the percentage of CR using the following the procedure.

1. Extract 1-10 g of the CRM asphalt binder using hot toluene extraction method described above.
2. On step 5: Exhaustively wash the crumb rubber on the filter papers with cold toluene until total removal of the dark asphalt color occurs.
3. Evaporate the toluene extracts to yield a mixture of the soluble rubber components and the asphalt binder. This can be analyzed by GPC as described above.
4. 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.

The procedure to detect percentage crumb rubber from an asphalt pavement core is different because the hot toluene extraction of the asphalt binder from the core fails to remove the insoluble crumb rubber from the mixture. The ignition method AASHTO T 308 for determination of asphalt content should be applied to assess the insoluble CR content as follows:

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

Comparative Evaluation of Large Scale CRM Binder Samples from Asphalt Pavement Cores using either Bromopropane or a Toluene/Ethanol Mixture

In this report CRM rubber modified asphalt samples were extracted using at toluene/ethanol mixture and the the amount of crumb rubber in the binder (the residue) was estimated gravimetrically. A literature report suggested that n-bromopropane is more effective solvent than an 85% toluene:15% ethanol mixture for extracting the soluble components from a crumb rubber modified asphalt cement. The relative efficiency of the two possible extraction solvents was compared in the following set of experiments.

Analysis of PG 82-22m CRM Asphalt Cement Sourced from Company B

Extraction using toluene/ethanol mixture:
Two extractions were done in a solvent mixture of 85% toluene: 15% ethanol (volumetric ratio).
Concentration: 2g/100mL

1. Extraction was done at *room temperature* by stirring the asphalt in the above solvent mixture for 2 hours. It was filtered through a pre-weighed Whatman filter paper (#5) using a Buchner funnel. After filtration, the filter paper along with funnel was dried in vacuum.

Weight of the sample taken = 2.39g
Solvent volume = 120 mL
Weight of the residue after filtration = 0.23g
% not dissolved = 9.6%
Solubility % = 90.4

2. Extraction was done by stirring and heating the solution to its boiling point and then reducing the temperature to room temperature. Rest of the procedure was as above.

Weight of the sample taken = 2.25 g
Weight of the residue after filtration = 0.21g
% not dissolved = 9.3%
Solubility % = 90.7

Extraction using n-propyl bromide:

1. 50 mL of n-propyl bromide was added to 1g of asphalt and dissolved by stirring and slightly warming the solution for one hour. Then it was filtered through a pre-weighed Whatman filter paper (#5) using a Buchner funnel. After filtration, the filter paper along with funnel was dried in a vacuum oven. Later, the dry filter paper was weighed.

Weight of the sample taken = 1g
Solvent volume = 50 mL
Weight of the residue after filtration = 0.0918g
% not dissolved = 9.2
Solubility % = 90.8

Conclusive results: It was observed that both bromopropane and toluene/ethanol mixture gave ~ 9% insoluble crumb rubber content. Since bromopropane is more expensive than toluene and ethanol, the toluene/ethanol mixture appears to be the best option, especially for large scale extractions.

DISCUSSION OF RESULTS

Gel Permeation Chromatography

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 GPC; there are many reports of asphalt separation by this method [*1-4*]. 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.

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 research, tetrahydrofuran (THF) was the solvent of choice. GPC chromatographs obtained using toluene as the solvent exhibited a lower resolution (see Table 4, Set 6 columns) and the differential refractive index between toluene and asphalt components was very small. Using the calibration curve (Figure 7), 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 the development and implementation of a standard procedure for using GPC as an analytical tool to define the percentage of polymer modifiers in polymer modified asphalt binders soluble in eluting GPC solvents.

Selection of the GPC System

The GPC system was chosen on the basis of the following criteria: (1) simplicity of operation, (2) robustness of components, (3) efficiency of polymer separation from asphalt components, and (4) speed of analysis. There are four different options for detecting the concentration of sample in the eluent: differential refractive index (RI), ultraviolet absorbance (UV), differential viscosity (VIS), and low angle light scattering (LALS). Asphalt samples were examined using all four detectors. However, the VIS detectors did not contribute sufficient new information and the LALS was judged unnecessary for routine PMAC analysis.

After reviewing the possible system options, the most cost effective GPC system proved to be the all in one system from Tosoh Bioscience. The EcoSEC system is a semi-micro design engineered for low volume separations. The complete system includes an auto-sampler, solvent purge and degasser, temperature controlled high pressure pumps, column oven, RI detector, and UV detector compacted into a single cabinet with a relative small footprint. The system also includes a data acquisition computer equipped with EcoSEC GPC Workstation Software. The column oven can hold up to eight 7.8mm ID x 30cm columns. More importantly, the high sensitivity of the DRI detector allows the use of 6.0mm ID x 15cm SuperH columns, which reduces the peak volumes and decreases the analysis time. Further, lower sample concentrations are required when the SuperH columns are installed so the tendency for solute aggregation is reduced.

Several 30 cm column combinations were evaluated to both maximize the separation of the polymer additive from the asphalt components and separation of the asphaltenes from the maltenes. 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 (Table 4). In this study, it was found that eluting with THF through Set 7 (Table 4) is the best combination of columns for GPC analysis at room temperature. The most effective corresponding shorter Super H column set proved to be one Super Hz 4000, pore size 200Ǻ, polystyrene MW range exclusion $4 \times 10^{5,}$ two Super Hz 3000, pore size 75Ǻ, polystyrene MW range exclusion 6×10^4 and one Super Hz 2500, pore size 30Ǻ, polystyrene MW range exclusion 2×10^4. Using sample concentrations of 0.25% and eluting at 0.35 mL/min, the total time for a sample analysis is reduced to less than 30 minutes. Samples subjected to GPC analysis can be injected at 30 minutes intervals as long as the sample tailing is minimal. **It is imperative to run duplicate measurements** and compare the results in order to detect any analytical errors in sample preparation and handling. To minimize errors in determining the content of polymer in asphalt samples by GPC technique due to the interactions of eluting solutions and column filling materials, the instrument should be calibrated with the cocktail set of polystyrene standards at least once a month.

Table 4
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			100-3K	500-6K	1K-15K	1K-75K	5K-500K	100-10,000 K	
	Solvent	Guard column							Test time min
SET1	THF	1			1		1	1	35
SET2	THF	1			1		1	1	35
SET3	THF	1	1	1		1			45
SET4	THF	1		1	1	1	1		45
SET5	THF	1			1	2			45
SET6	THF	1				2	1		45
SET6	Toluene	1				2	1		50
SET7	THF	1			1	1	1	1	50

GPC Analysis of Molecular Weight Distribution of SBS Polymer from Different Sources

The SBS copolymer is one of the most common polymers added to asphalt to produce PMAC. In order to understand the molecular weight distribution of this polymer, three SBS polymers obtained from different sources were analyzed. The resulted chromatograms presented in Figure 13 clearly show that different companies supply SBS polymers with different molecular weight distributions. All polymeric species show up in the high molecular weight region of the chromatogram and do not overlap with asphalt components of much lower MW (molecular weight). Thus determining the amount of polymer in a PMAC is feasible when using a high-resolution column system such as the SuperH column set of the Tosoh instrument from the DOTD Materials Laboratory.

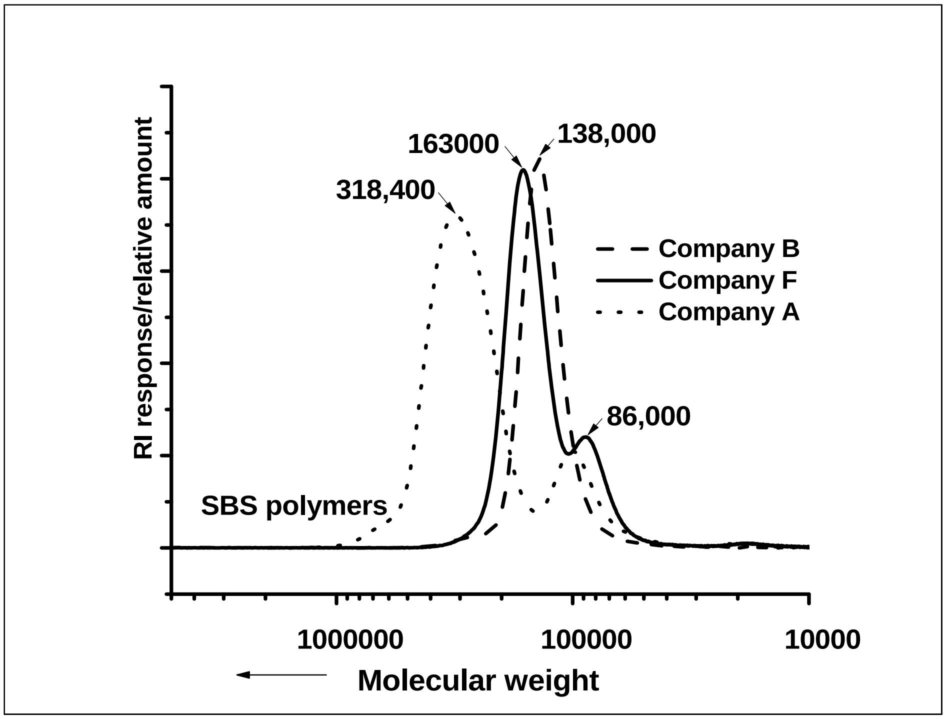


Figure 13

Molecular weight distribution of SBS polymer from three different sources

To estimate the accuracy of this analysis of the percentage of polymer in an asphalt mixture, different known amounts of SBS polymer were mixed with a polymer free asphalt and then subjected it to GPC analysis.

Table 5
Relative concentrations of components in spiked SBS asphalt mixtures

	1000K - 300K %	300K – 45K %	45K-19K %	Total polymer (%)	Asphaltene (%)	Maltene (%)
ASPHALT	0	0	0.034	0.034	17.48	82.48
ASPHALT + 1% SBS	0.72	0.18	0.09	0.99	17.24	81.77
ASPHALT + 2% SBS	1.46	0.43	0.13	2.03	17.17	80.80
ASPHALT + 5% SBS	3.48	1.08	0.20	4.76	16.77	78.47
ASPHALT + 10% SBS	7.77	2.46	0.28	10.51	15.87	73.61

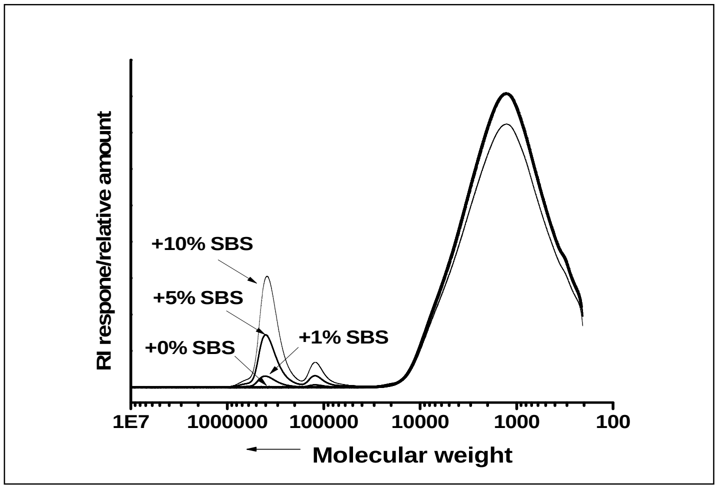


Figure 14
GPC chromatograms of asphalts spiked with SBS polymer (Company A)

A 1% solution of asphalt and a 1% solution of SBS polymer was prepared in THF in two separate vials and were kept overnight for dissolution. The next day, the solutions were mixed to get solutions of 1%, 2%, 5%, and 10% concentration, respectively, of polymer in asphalt. These solutions were filtered using 0.45µ filters into a 2ml vial and analyzed. The chromatograms obtained are shown in Figure 14. The data was analyzed to determine the percentage amounts of polymer, asphaltenes and maltenes. The results were tabulated in Table 5. The conclusion was that the GPC technique could reveal the actual amount of polymer present in the asphalt/SBS blends.

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.

Given that the GPC conditions are equal, characteristic chromatograms for Louisiana asphalt sources can be obtained. The data were collected at DOTD materials laboratory over a two year interval from differing sources. The content of polymer in binders sourced from different companies (refineries and contractors) labeled as PG 76-22m PG-76m data is compiled in Table 6. A similar compilation for binders labeled as PG-70-22m is reported in Table 7. The compositions of the most common PG 67-22 and PG 64-22 binders are reported in Table 8.

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. In general this is the case. However, when perusing the data compiled in Table 6, one can see that occasionally PG 76-22m binders contained less than 2% polymer. Correspondingly, review of the data in Table 7 reveals samples with only a 0.50% polymer content in some of the PG 70-22m asphalts analyzed. These findings should be immediately taken as an indicator that the respective binders should be tested in order to verify the actual performance grade.

Table 6
Polymer content of PG 76-22m asphalt cements from different sources determined by GPC analyses routinely run at the DOTD Material Laboratory

PG 76-22m Asphalts Source	**Run 1 Polymer %**	**Run 2 Polymer %**	**Mean Polymer %**
Company A	3.50	3.60	3.55
Company A	2.78	2.48	2.63
Company A	2.34	2.35	2.34
Company A	3.48	3.07	3.27
Company A	3.05	3.47	3.26
Company A	2.49	2.35	2.42
Company A	2.47	2.18	2.33
Company A	2.73	2.44	2.59
Company A	3.12	3.26	3.19
Company A	2.55	2.52	2.54
Company A	2.53	2.51	2.52
Company A	3.93	4.04	3.99
Company A	2.57	2.92	2.75
Company A	2.26	2.84	2.55
Company A	2.56	2.65	2.61
Company A	2.17	2.93	2.55
Company A	2.96	2.8	2.88
Company A	2.68	2.79	2.74
Company A	3.08	2.78	2.93
Company B	3.46	3.35	3.41
Company B	3.77	3.69	3.73
Company B	3.14	2.88	3.01
Company B	3.53	3.76	3.65
Company B	3.96	3.24	3.60
Company B	3.63	3.48	3.55
Company B	3.66	3.64	3.65
Company B	4.18	4.25	4.21
Company B	3.77	3.78	3.78

Company B	3.24	2.62	2.93
Company B	4.22	3.62	3.92
Company B	4.17	3.63	3.90
Company B	4.12	4.05	4.09
Company B	3.66	3.35	3.50
Company B	3.82	3.48	3.65
Company B	3.44	3.22	3.33
Company B	3.6	3.78	3.69
Company B	3.78	3.32	3.55
Company B	3.71	3.54	3.63
Company B	3.84	3.69	3.76
Company B	3.32	3.83	3.58
Company B	3.38	3.78	3.58
Company B	3.86	3.67	3.76
Company B	3.42	3.36	3.39
Company B	3.69	3.55	3.62
Company B	3.58	3.76	3.67
Company B	3.9	3.77	3.84
Company B	3.04	3.17	3.11
Company B	2.9	3.11	3.00
Company B	3.71	3.48	3.59
Company B	3.23	3.17	3.20
Company B	**1.45**	**1.52**	**1.48**
Company B	3.93	3.95	3.94
Company B	3.46	3.64	3.55
Company B	3.22	3.54	3.38
Company B	3.26	3.55	3.40
Company B	3.45	3.62	3.54
Company B	3.36	3.63	3.50
Company B	3.2	3.43	3.32
Company B	4.08	3.4	3.74
Company B	4.1	3.65	3.88
Company B	3.86	3.36	3.61
Company B	3.84	3.42	3.63
Company B	3.61	4.42	4.01
Company B	3.38	3.41	3.40

Company B	3.67	3.87	3.77
Company B	3.47	3.85	3.66
Company B	3.6	3.54	3.57
Company B	3.69	3.59	3.64
Company B	3.71	4.02	3.86
Company B	3.62	3.49	3.56
Company B	3.56	3.73	3.65
Company B	3.89	4.02	3.96
Company B	3.53	3.75	3.64
Company B	3.84	3.77	3.80
Company B	3.38	3.44	3.41
Company B	3.49	4	3.75
Company B	3.17	3.22	3.20
Company B	2.81	2.5	2.66
Company B	3.35	3.26	3.30
Company B	3.79	3.65	3.72
Company B	3.45	3.28	3.37
Company B	3.26	3.74	3.50
Company B	3.58	3.61	3.59
Company B	3.12	3.31	3.21
Company B	3.61	3.5	3.55
Company B	3.55	3.42	3.48
Company C	3.6	3.41	3.50
Company C	3.23	3.74	3.49
Company C	3.87	4.06	3.96
Company C	3.51	3.91	3.71
Company C	**2.05**	**1.82**	**1.93**
Company C	3.24	3.34	3.29
Company C	4.23	3.29	3.76
Company C	3.32	3.16	3.24
Company C	3.49	3.80	3.64
Company C	3.38	3.46	3.42
Company C	3.25	3.33	3.29
Company C	3.35	3.13	3.24
Company C	3.18	3.33	3.25

Company C	3.12	3.33	3.23
Company D	3.54	3.06	3.30
Company D	3.6	3.82	3.71
Company D	3.32	3.17	3.25
Company E	4.25	4.68	4.46
Company F	3.54	3.64	3.59
Company F	4.01	4.22	4.12
Company G	2.67	3.39	3.03
N/A	3.45	3.2	3.33

Table 7
Polymer content of PG 70-22m asphalt cements from different sources determined by GPC analyses routinely run at the DOTD Material Laboratory

PG 70-22m Asphalts Source	**Run 1 Polymer %**	**Run 2 Polymer %**	**Mean Polymer %**
Company A	1.6	1.39	1.50
Company A	1.88	1.41	1.65
Company A	1.22	1.16	1.19
Company A	1.6	2.42	2.01
Company A	1.98	1.51	1.75
Company A	1.98	2.1	2.04
Company B	2.17	1.71	1.94
Company B	0.5	0.54	0.52
Company B	1.54	1.67	1.61
Company B	1.91	1.58	1.75
Company B	**0.57**	**0.43**	**0.50**
Company B	2	2.43	2.21
Company B	1.57	1.44	1.50
Company B	1.75	1.89	1.82
Company B	1.61	1.69	1.65
Company B	1.52	1.39	1.46
Company B	1.47	1.47	1.47
Company B	1.66	1.7	1.68
Company B	1.69	1.25	1.47
Company B	2.65	2.67	2.66
Company B	1.48	1.43	1.46
Company B	1.96	1.85	1.91
Company B	2.06	2.07	2.06
Company B	2.1	2.34	2.22
Company B	1.51	1.96	1.73
Company B	1.48	1.65	1.56
Company B	2.53	2.42	2.48
Company B	1.95	1.81	1.88

Company B	2.05	2.01	2.03
Company B	1.15	0.76	0.95
Company B	1.46	1.42	1.44
Company B	1.13	1.38	1.25
Company B	**0.46**	**0.59**	**0.53**
Company B	1.65	2.07	1.86
Company B	2.47	2.24	2.36
Company B	1.79	1.72	1.75
Company B	1.83	2.08	1.96
Company B	1.78	1.84	1.81
Company B	1.73	1.39	1.56
Company C	1.31	1.55	1.43
Company C	1.65	1.73	1.69
Company C	**0.86**	**0.53**	**0.70**
Company C	1.82	1.43	1.63
Company C	1.64	1.72	1.68
Company C	1.87	1.88	1.88
Company C	2.74	2.31	2.53
Company C	1.73	1.81	1.77
Company C	1.51	2.54	2.02
Company D	1.7	2	1.85
Company D	1.77	1.82	1.79
Company D	2.02	1.84	1.93
Company D	2.25	2.14	2.20
Company D	2.44	1.68	2.06
Company D	2.23	1.83	2.03
Company D	2.7	1.72	2.21
Company D	1.94	2.32	2.13
Company D	2.23	1.95	2.09
Company E	4.83	4.93	4.88
Company E	4.83	4.93	4.88
Company E	2.55	1.45	2.00
Company E	2.39	2.16	2.28

Company E	2.21	1.7	1.96
Company E	2.18	2.07	2.13
Company E	2.02	1.69	1.86
Company F	1.54	1.65	1.60
Company F	1.84	2.4	2.12
Company H	2.37	2.37	2.37
Company H	2.37	2.39	2.38

Table 8
Polymer content of PG 67-22 and 64-22 asphalt cements from LA sources determined by GPC analyses routinely run at the DOTD Material Laboratory

PG and Asphalts Source	**Run 1 Polymer %**	**Run 2 Polymer %**	**Mean Polymer %**
Company B PG 67	0.23	0.29	0.26
Company J PG 64	0.72	0.65	0.69

Forensic Applications of GPC Analysis

The compilation of GPC data on the asphalt cements supplied to the DOTD can be used to compare these initial analyses with data obtained from cores extracted in the field. Application of GPC for assessment of the extent of oxidative aging of modified asphalt binders as well as forensic analysis of pavement failures has been investigated extensively. The following specific examples illustrate this application..

GPC Analysis of the Binder Extracted from LA 146 Calumet Rd. and of the Related Asphalt Emulsion

An emulsion asphalt sample, supposedly the original binder used by contractor for paving the LA 146 Calumet Road, stored in a gallon can, was analyzed in order to determine the asphalt composition. The asphalt emulsion stored in the container was phase separated into two layers: a lower solid phase and an upper liquid phase. Both phases have been analyzed separately. GPC data of the extracted paving asphalt have been compared with that of the two emulsion phases separated in the container. The results are shown in Figure 15 and Table 9. The can asphalt samples (separated solid phase and liquid phase) had nearly the same content of asphaltenes and maltenes species, while the amount of polymer was slightly higher in the solid deposit. However, the content of polymer and asphaltenes was higher in the road extract, with a corresponding lower percent amount of maltenes which had also the mean MW centered to a lower molecular weight of around 1,000 Daltons (Figure 15). At the same time, the GPC traces of the two can asphalt phases are almost identical, while the chromatogram of the LA 146 Calumet Road extract is very different from these two, raising the question if the emulsion forwarded for GPC analysis was actually the same with the binder used for road paving.

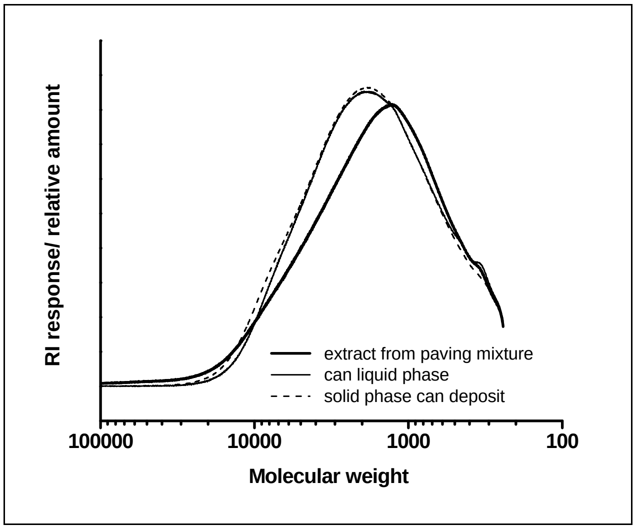


Figure 15

Comparison between GPC traces of the LA 146 Calumet road core extract and that of the liquid and solid phases separated in the original emulsion of the paving asphalt binder

Table 9

Comparison between GPC data of the LA 146 Calumet road core extract and that of the liquid and solid phases separated in the original emulsion of the paving asphalt binder

Sample	1M-300K %	300-45K %	45-19K %	% Total Polymer	Asphaltenes %	Maltenes %
LA-146 Extract	0.09	0.11	0.39	0.59	23.90	75.51
Emulsion deposit	0.02	0.06	0.28	0.36	22.40	77.24
Emulsion liquid part	0	0	0.04	0.04	22.21	77.75

Analysis of I-12 Pavement Failures

At the request of District 62 and the Materials Section, LTRC personnel performed a site investigation of the entire project located near Covington, LA on September 15, 2010. The photograph presented below shows the presence of surface holes. The extent of this problem seems to be limited to the west side of the project, outside lane, inside wheel path. There was not a fixed count, but a rough estimate was approximately 10 full depth holes ranging from 2 inches to 6 inches in diameter.

Figure 16
Typical surface holes

LTRC sent the coring crew to investigate and took five cores westbound and five cores eastbound. The asphalt cores were extracted and the gradation and AC content was determined to be similar to the design. Two test samples, one east bound and one west bound, resulted in 6.3 and 6.4% asphalt cement content, respectively, from the ignition oven extraction.

A core from I-12E was heated at 65°C for 30 minutes to facilitate fragmentation into the coated aggregated components. We noted that the aggregates did not break up readily and clumps of crumb rubber were observed. The rubber clumps were much larger than one would expect in 40 mesh CRM. The rubber clumps could be broken up by hand crushing. The existence of these rubber clumps suggests that the CRM was not completely dispersed in the liquid binder.
The aggregate mixture remaining after toluene extraction still contained large clumps. The clumps appeared to be fines that were stuck together so effectively that the hot toluene failed to penetrate them. The clumps were cleaved by striking with a hammer and the fracture surfaces appeared to be composed of fines. The results suggested that two problems were present. One, the CRM was not properly dispersed in the asphalt binder. Two, the aggregates contained a large fraction of fines that formed large clumps when mixed with the binder.

The coated aggregates with extracted with hot toluene. The extract was allowed to settle to allow the fines to separate, the supernatant was centrifuged and the resultant clear toluene solution was evaporated under reduced pressure. A sample of the binder thus recovered was dissolved in THF for GPC analysis. The GPC traces of the binder are shown below along with a binder extracted with an I-55 S-bound core (Figure 17). The chromatograms and the percent fraction weight of the major components were very similar. As seen in Table 10, The binder from I-12 shows normal % composition of soluble rubber, asphaltenes and maltenes, completely analogous to that of the I-55 S-bound which is performing well.

Table 10

Comparison between asphalt composition of samples taken from road pavements of I-55 S and I-12 E Highways

No.	Site	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer MW	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K	Total
19	I-55 S bound core	0.0%	0.5%	2.6%	3.1	18%	79%	100%
18	I-12 E bound core	0.1%	0.7%	2.3%	3.1	17%	80%	100%

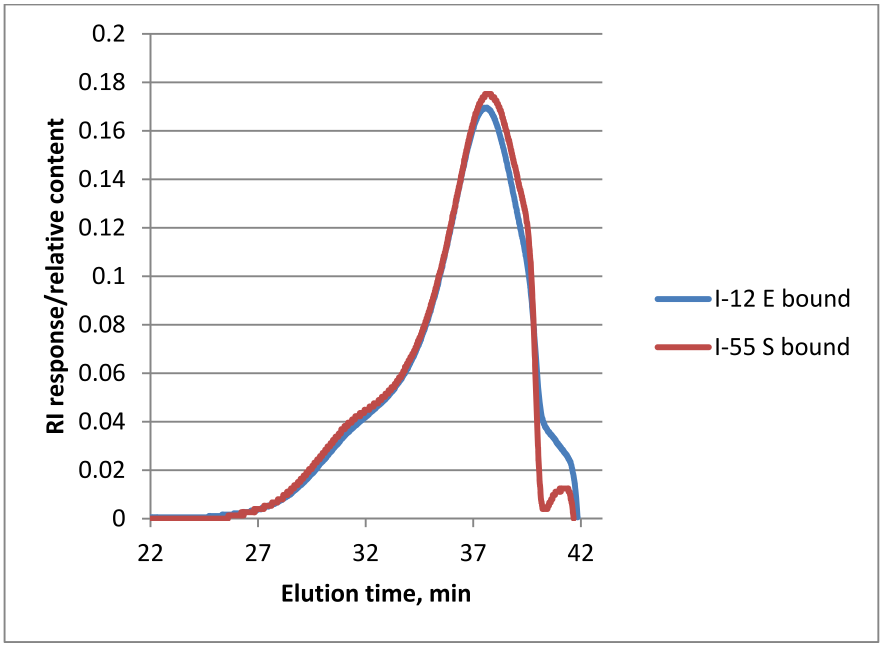


Figure 17

Comparison between GPC traces of I-12 E bound and I-55 S bound asphalts

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These results prompted however a more in-depth GPC analysis of I-12 pavement samples. The mean composition of asphalts extracted from cores taken from road pavements of I-12 East Bound and of I-12 West Bound are presented in Tables 11 and 12, respectively.

Table 11
Asphalt composition of samples taken from road pavements of I-12 East Bound (mean values)

Asphalt	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer MW	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
Good pavement section	0.09	0.30	0.69	1.08	14.26	84.66
Bad pavement section	0.11	0.97	2.94	3.96	20.20	75.84

Table 12
Asphalt composition of samples taken from road pavements of I-12 West Bound (mean values)

Asphalt	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer MW	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
Good pavement section	0.05	0.56	2.35	2.96	19.41	77.63
Bad pavement section	0.08	0.76	2.77	3.62	20.20	76.18

The data of individual samples for which the means for I-12 East Bound and I-12 West Bound compositions were determined are presented in Tables 13-16 below.

Table 13
Asphalt from I-12 good pavement section East Bound GPC data

Sample	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer MW	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
A14	0.26	0.57	0.67	1.50	14.22	84.27
A15	0.01	0.17	0.72	0.90	14.41	84.65
A16	0.00	0.15	0.69	1.08	14.26	84.66

Table 14
Asphalt from I-12 bad pavement section East Bound GPC data

Sample	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer %	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
A9	0.08	0.73	2.82	3.63	20.74	75.63
A11	0.14	1.15	3.21	4.50	19.78	75.72
A13	0.10	0.87	2.78	3.75	20.07	75.84

Table 15
Asphalt from I-12 good pavement section West Bound GPC data

Sample	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer MW	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
A5	0.03	0.55	2.08	2.88	18.39	78.94
A6	0.10	0.60	2.64	3.34	20.31	76.35
A8	0.02	0.53	2.33	2.88	19.54	77.67

Table 16
Asphalt from I-12 bad pavement section West Bound GPC data

Sample	VHMW 1000-300K	HMW 300-45K	MMW 45-19K	SUM Polymer MW	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
A1	0.10	0.82	2.65	3.57	19.36	77.07
A3	0.08	0.70	2.64	3.42	20.14	76.44
A4	0.07	0.76	2.77	3.62	20.20	76.18

The most significant difference between the good and the bad pavement section is the high concentration of medium molecular weight polymer (MMW) and a higher concentration of asphaltenes. This change could have been the result of excessive heating during the mixing of the binder with the aggregate, which lead to thermal degradation of the crumb rubber.

The source of the excess heating could be overheating of the aggregate during the drying process prior to addition of the binder. To test this hypothesis, a series of PG 82-22m CR asphalts extracted from mixtures similar to that of I-12 pavements prepared by the contractor by heating the aggregate at increasing temperatures, i.e. from 325 to 550°F, before adding the binder. GPC data on the extracts of these test samples are presented in Table 17 and Figure 18.

Table 17
GPC Composition of PG 82-22m CRM asphalts extracted from mixtures prepared by heating the aggregate at different temperatures

No	Aggregate Temp °F	1000K - 300K %	300K – 45K %	45K-19K %	Total polymer (%)	Asphaltenes (%)	Maltenes (%)
1	325	0.12	1.12	2.10	3.34	23.88	72.77
2	450	0.09	1.07	2.35	3.51	24.48	72.01
3	550	0.14	1.62	3.6	5.36	25.85	68.79

In each case the mixutures contained unusually high concentrations of MMW and asphaltene components. Heating the aggregate to 550°F effects a degradation of CRM as reflected by a pronounced increase of both the polymer and asphaltenes contents, with a concomitant decrease in the maltene content. The changes in binder composition might indeed downgrade the mixture paving properties. These results suggest that control of the aggregate temperature is a critical variable to consider.

However, no conclusive phenomena have been found responsible for the I-12 distress. Since the extent of the problem has probably been defined, and the frequency of additional pop-outs diminished, it has been recommended that the pavement be patched as the problem occurred.

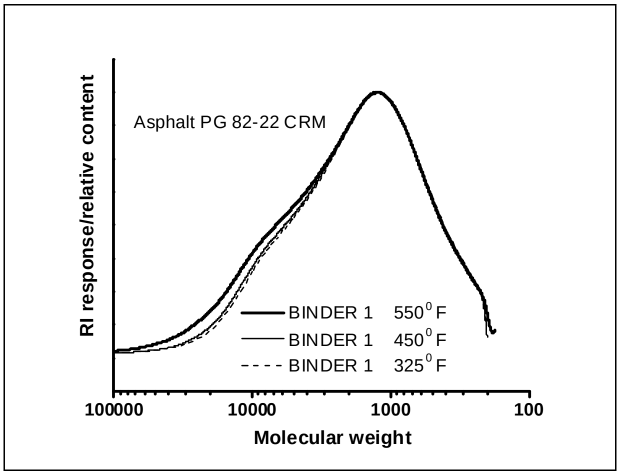

Figure 18
The influence of aggregate temperature on composition of PG 82-22m CRM asphalts extracted from mixtures prepared by heating the aggregate at different temperatures

Impact of RAP Blending into Road Pavements

GPC Analysis of Binders Extracted from US 171 Hwy

An analysis has been made for two asphalt materials extracted from US 171 road pavements containing reclaimed asphalt pavement of different amounts: 15%RAP Conv. Madden and 30% RAP Foamed Madden. Unexpectedly, the amounts of asphaltenes and maltenes in the two samples were very close. A substantially higher asphaltene content was expected in the RAP Foamed Madden sample since it contained twice as much RAP. Further, the polymer content (MMW in particular) was higher for the foamed binder containing 30% RAP. A higher extent of asphaltene aggregation lead to an overlapping of high MW asphaltenes with MMW polymers species (viz., overlapping of species eluting in the >19K molecular weight region of the GPC chromatogram). Thus the apparent increase in polymer concentration in the RAP Foamed Madden can be attributed to aggregated asphaltenes at the 30% RAP concentration. These findings should be correlated with physical data regarding these particular US 171 pavements (in further research projects). The GPCresults are presented in Table 18.

Table 18

GPC results of US 171 Hwy road pavements containing reclaimed asphalt pavement of 15%RAP Conv. Madden and 30% RAP Foamed Madden

Site	VHMW 1M-300K	HMW 300-45K	MMW 45-19K	SUM Polymer	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
US 171 30% RAP Foamed Madden	0.0%	1.5%	4.5%	6.0	16.0%	78.0%
US 171 15% RAP Conv. mix Madden	0.0%	1.4%	2.3%	3.7	17.0%	79.3%

GPC Analysis of Binders Extracted from LA 116 Hwy

A comparison has been made between the asphalt compositions of two asphalt materials extracted from LA 116 cores, the difference between the sites of origin being the amount of reclaimed asphalt pavement used: LA 116 15% RAP Conv. Diamond B versus LA 116 20% RAP Conv. Diamond B (Figure 19). As shown by data listed in Table 19, a higher RAP content in the paving mixture (15% versus 20%) is reflected in an expected higher amount of asphaltenes (22% for 20% RAP versus 16% for 15% RAP) in the binder. At the same time, the sum of polymeric species was also higher for the 20% RAP mix (3.4% versus 2.9% for 15% RAP), due perhaps to the polymer originating from the PMAC still present in the RAP asphalt composition and/or of the overlapping of high MW asphaltenes aggregates with MMW polymers as described above.

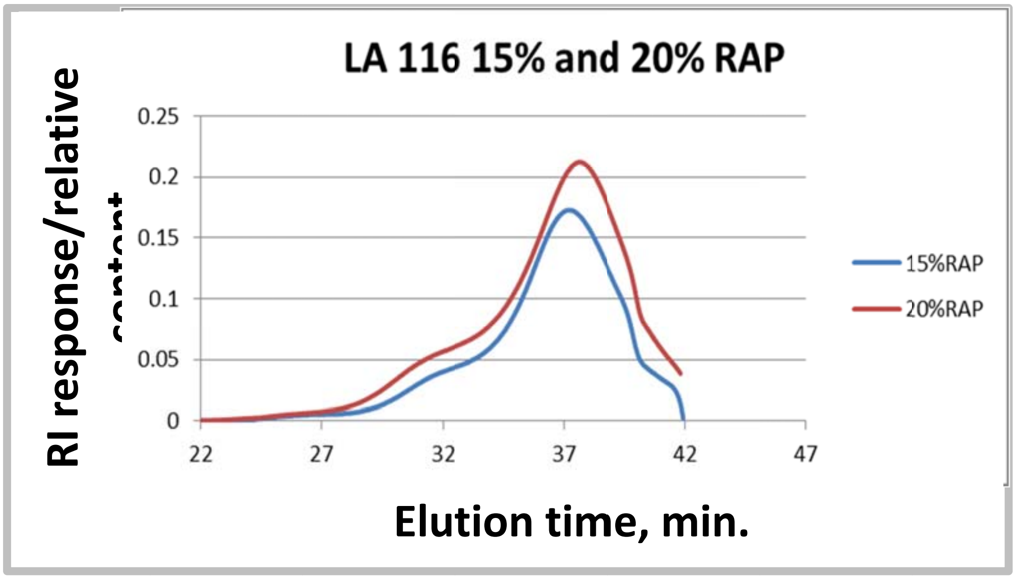

Figure 19
GPC traces of 15% RAP and 20%RAP asphalt materials extracted from LA 116 cores

Table 19
GPC results of 15% RAP and 20%RAP asphalt materials extracted from LA 116 Hwy cores

Site	VHMW 1M-300K	HMW 300-45K	MMW 45-19K	SUM Polymer	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
La 116 15% RAP conv. mix Diamond B	0.0%	1.2%	1.7%	2.9%	16%	81%
LA 116 20% RAP conv. mix Diamond B	0.1%	1.1%	2.1%	3.4%	22%	75%

Correlation between Stiffness of Asphalt Cements and Asphaltenes Content

Table 20 presents the characterization of two 70-22m base asphalt cements which have been used for paving of US 171 and LA 116 roads. The pavements of these roads contain 20% RAP. LA 116 base asphalt was latex modified PG 70-22m. The GPC analysis of the road extract (with the contribution of the asphalt from 20% RAP) indicated that the asphaltenes fraction was 16%

(Table 21). The asphaltenes content of the US 171 road extract was found to be 17%. There was also a difference between the content of polymeric species between these two road extracts, which was rather higher for the US 171 extracted material (Table 21 and Figure 20). While physical data for cores sampled from the roads were not available, given the fact that the RAP content was the same (20%), one may try to make a correlation between GPC data of road material extracts and SUPERPAVE characterization data of base asphalts. To this aim, it is worth correlating the bending beam (BBR) creep stiffness at -12°F of base asphalt cements listed in Table 20 with the content of asphaltenes from Table 21: a higher content of asphaltenes for US 171 paving asphalt (17% vs. 16% of LA 116 extract) is reflected in an increased BBR stiffness for US 171 paving extract (168.0 MPa vs. 157.8 MPa of LA 116 material).

At the same time, despite the higher content of polymeric species for US 171 Original Binder PG 70-22m (3.7%) versus that of LA 116 Latex modified PG 70-22m (2.9%), higher values have been recorded for the rheology of the latex modified asphalt cement, viz., for rotational viscosity at 135°C, for G*, G*/Sinδ of original and G*/Sinδ of RTFO treated material, all determined at the grading temperature of 70°C. As a good correlation with BBR results, a stiffer binder resulted after the PAV aging of the US 171 Original Binder when G* Sin δ at 25°C data are compared, i.e., 4300 MPa versus the much lower 3078 MPa for LA 116 latex modified asphalt cement (Table 20).

Table 20
SUPERPAVE characterization of original and latex modified PG 70-22m asphalt binders

No.	TEST NAME	US 171 (Original Binder PG 70-22m)	LA 116 (Latex modified PG 70-22m)
1	Rotational Visc. (Pa-s) @ 135°C	0.85	1.60
2	Original DSR, G* (kPa) @ 70°C	1.51	1.90
3	Original Phase Angle, δ (°) @ 70°C	82.00	75.00
4	Original G*/Sinδ (kPa) @ 70°C	1.52	2.60
5	RTFO DSR, G* (kPa) @ 70°C	2.65	3.70
6	RTFO Phase Angle, δ (°) @ 70°C	76.51	72.40
7	RTFO G*/Sinδ (kPa) @ 70°C	2.73	3.88
8	PAV G* x Sin δ (kPa) @ 25°C	4300	3078
9	BBR Creep Stiffness (MPa) @ -12°C	168.0	157.6
10	BBR Creep Slope m @ -12°C	0. 320	0.301

Table 21
GPC results of 15% RAP asphalt materials extracted from LA 116 Hwy and LA 171 Hwy cores

ASPHALT	VHMW 1M-300K	HMW 300-45K	MMW 45-19K	SUM Polymer	Asphaltenes 19-3.5K	Maltenes 3.5-0.2K
LA 116 Extract (15% RAP)	0.0%	1.2%	1.7%	2.9%	16.1%	81.0%
US 171 Extract (15% RAP)	0.0%	1.4%	2.3%	3.7	15.2%	81.1%

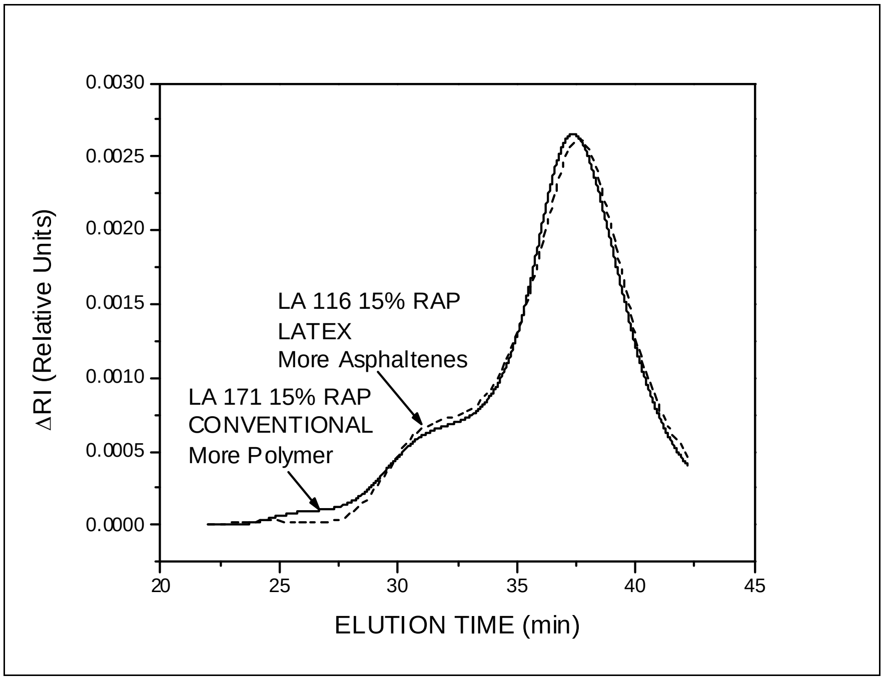

Figure 20
GPC traces of 15% RAP asphalt materials extracted from US 171 and LA 116 cores

GPC Data of a Warm Mix Asphalt Additive and of Related Paving Materials

At the request of LTRC an asphalt additive blend for WMA (Proline) and mixtures containing Proline (Proline limestone and Proline gravel) have been analyzed. No additional data have been provided for these samples, such as the Proline content in the mixtures. The results are listed in Table 22 and individually presented in Figures 21-23. The rather high content of asphaltenes in the Proline additive as well as its polymer content should be noted.

Table 22
GPC results of Proline sample, Proline Limestone, Proline Gravel

Sample	1000K - 300K %	300K – 45K %	45K-19K %	**Total polymer (%)**	**Asphaltenes (%)**	**Maltenes (%)**
Proline	0	1.19	2.75	3.94	25.05	71.01
Proline Limestone	0.00	0.37	1.24	1.61	16.42	81.96
Proline Gravel	0	0.38	1.13	1.51	15.48	83.01

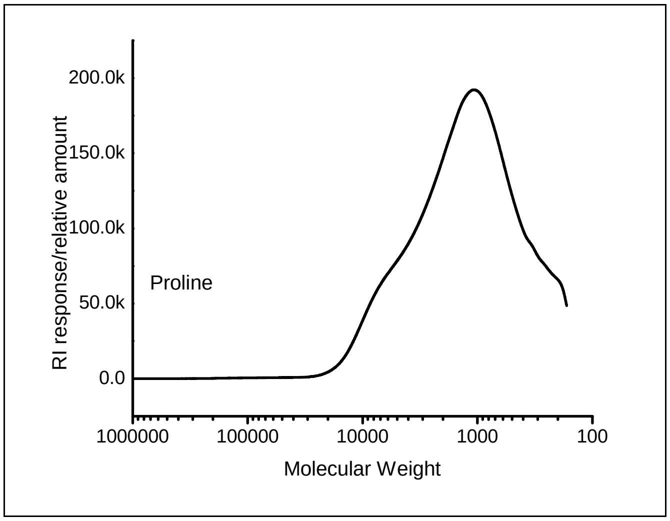

Figure 21
GPC trace for Proline sample

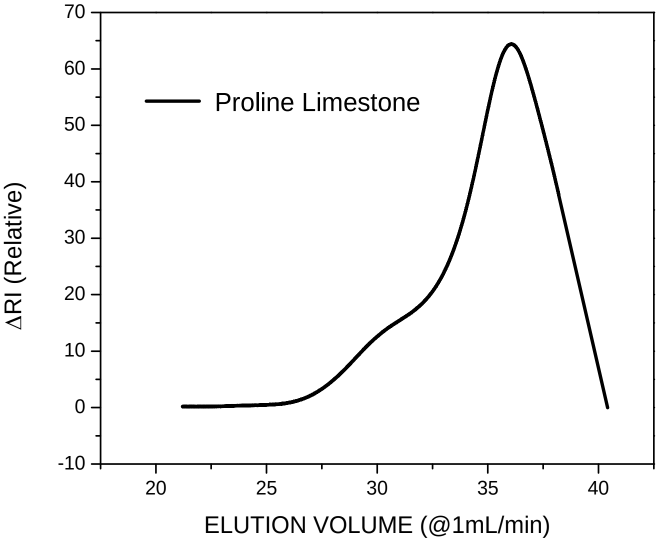

Figure 22
GPC data for Proline Limestone sample

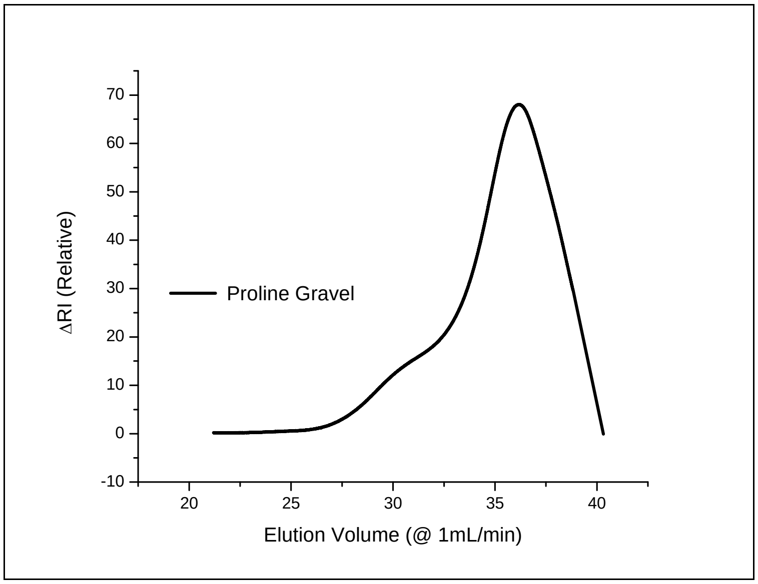

Figure 23
GPC data for Proline Gravel sample

GPC Data of Asphalt Binders obtained from Two Locations of Same Company as Compared to that of the Asphalt Extracted from LA 680 Road Pavement

The composition of asphalt binders obtained from two different locations of Company C varies. GPC data can be used to identify the source of the binder used to prepare the asphalt cement extracted from a road where a Company C binder has been used for paving... The Company C asphalt binders obtained from two different locations proved to have a totally different distribution of the asphaltenes and maltenes content (Table 23). The C1 asphalt had an unusual distribution of maltenes, i.e., likely it is "spiked" with low molecular species (MW <1,000 Daltons, Figure 24). The "spiked" maltenes content is more evident in the GPC traces of the asphalt extracted from LA 680 road, indicating in a forensic analysis that the C1 binder was indeed used for paving this roadway.

Table 23
GPC composition of asphalt binders obtained from two locations of same supplier (Company C) and of the road extract

Sample Source	1000K - 300K %	300K – 45K %	45K-19K %	**Total (%) polymer**	**Asphaltenes (%)**	**Maltenes (%)**
Company C1	0.01	0.13	1.58	1.73	25.09	73.18
Company C2	0	0.22	0.96	1.19	23.41	75.36
LA 680 Rd Extract	0	1.19	2.75	3.94	25.05	71.01

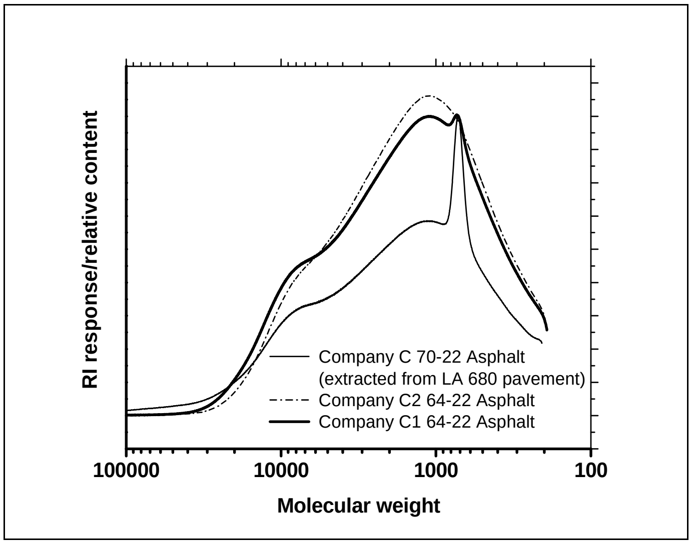

Figure 24

Super imposed GPC traces of: Company C asphalt extracted from LA 680 pavement, Company C1 asphalt and Company C2 asphalt binders

GPC Analysis of the Same Grade Asphalt from Three Different Sources

The results of this analysis, presented in Figure 25 and Table 24, point to the fact that the composition of base asphalt binders (PG 64-22) is different when sourced from different Louisiana supplying companies.

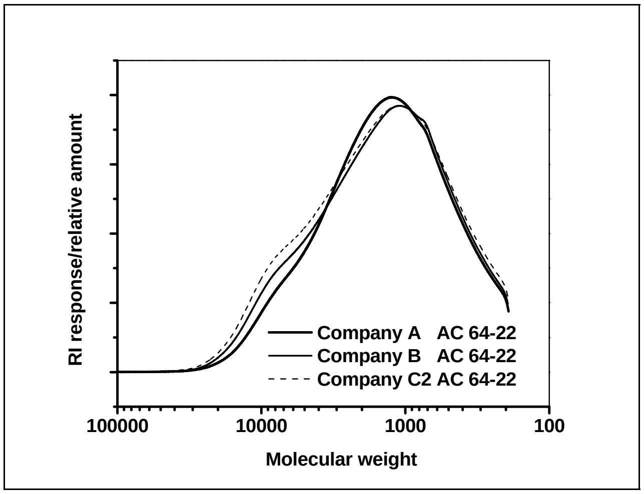

Figure 25

GPC traces of three 64-22 asphalts sourced from different companies

Not only that the contents of asphaltenes and maltenes are dissimilar, but also shows the presence of high molecular polymeric species (>45K – 19K) in a base asphalt of PG 64-22, which supposedly should not contain any polymer (Company C2 case). The percentage amount of asphaltenes is lowest in the asphalt sample sourced from Company A, which has also the highest maltenes content. The varied binder composition must be considered when calculating the amounts of polymers needed to be added in order to prepare higher asphalt grades, viz., PG 70-22m and PG 76-22m binders. Some examples are presented in Figure 26 and 27 and in Tables 25 and 26, respectively. For example, even if the GPC traces of PG 70-22m and PG 76-22m binders presented in Figures 26 and 27 are very similar and almost superimposed, their molecular composition is different. A total amount of 2.50% polymer was present in the PG 76-22m binder from Company A (asphaltenes content of 16.06%) as compared to 3.98% polymer for the asphalt binder of the same grade sourced from Company B, which had a higher asphaltenes content both in the base asphalt (Table 24) and in the PMAC (Table 26). (See also Tables 6 and 7 for additional data regarding the percent polymer content, binder grades, and suppliers).

Table 24
GPC composition of 64-22 asphalts sourced from different companies

PG 64-22 AC Source	1000K - 300K %	300K – 45K %	45K-19K %	**Total polymer (%)**	**Asphaltene (%)**	**Maltene (%)**
Company A	0	0	0.22	**0.22**	**19.44**	**80.34**
Company B	0	0	0.6	**0.6**	**21.81**	**77.59**
Company C2	0	0.22	0.96	**1.19**	**23.41**	**75.36**

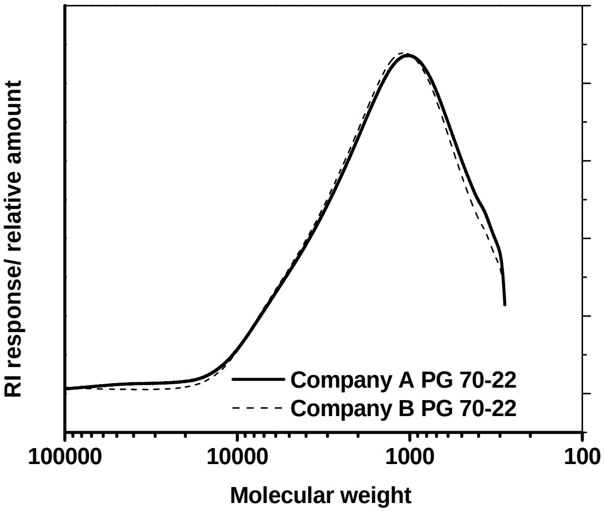

Figure 26
GPC traces of two 70-22m asphalts sourced from different companies

Table 25
GPC composition of 70-22m asphalts sourced from different companies

PG 70-22m AC Source	1000K - 300K %	300K – 45K %	45K-19K %	**Total polymer (%)**	**Asphaltenes (%)**	**Maltenes (%)**
Company A	0.02	1.01	1.19	2.22	17.69	80.09
Company B	0	1.04	0.51	1.54	17.88	80.58

Table 26
GPC composition of 76-22m asphalts sourced from different companies

PG 76-22m AC Source	1M - 300K %	300K – 45K %	45K-19K %	**Total polymer (%)**	**Asphaltene (%)**	**Maltene (%)**
Company A	0.06	1.69	0.74	**2.5**	**16.06**	**81.44**
Company B	0.29	2.93	0.76	**3.98**	**17.36**	**78.66**

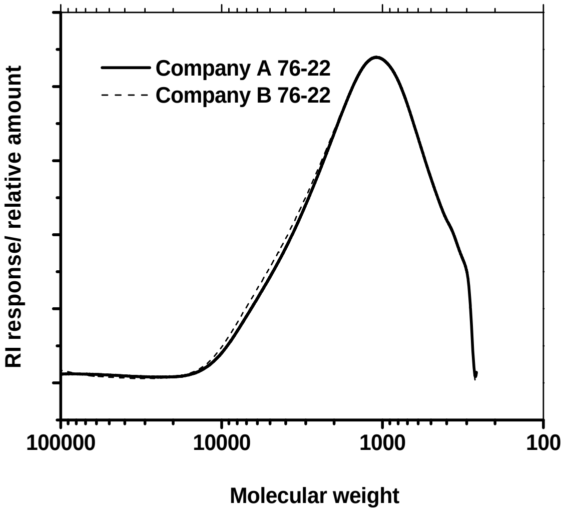

Figure 27
GPC traces of two 76-22m asphalts sourced from different companies

Analysis of Different Grades of Asphalts Obtained from FHWA

In order to enlarge the collection of GPC data for different types of asphalts of known composition, different grades of asphalt have been obtained from FHWA. The analysis of samples was carried out using the same conditions as described above. Figure 28 shows the superimposed chromatograms of these samples and Table 27 gives the details of percentages polymer, asphaltenes and maltenes present in these samples.

The chromatograms of Figure 28 demonstrate the capability of GPC to distinguish different types of asphalts. FHWA SBS 64-40 and FHWA SBS LG show the presence of added polymer. FHWA SBS 64-40 seems to contain a lower amount of high molecular weight polymer compared to SBS LG. FHWA air blown asphalt is definitely different from others in its MWD. It shows a highest percentage of asphaltenes compared to other three samples (Table 27). Air blown asphalts are made by blowing air through the binder at high temperature for four to five hours. Reports show that the amount of asphaltenes content increases because during heating under air, saturated molecules and non-polar aromatics are converted to resins and then the resins converted into asphaltenes. Thus GPC can identify air blown materials or PMAC's very easily by studying the percentages of polymer, asphaltenes, and maltenes.

Analysis RTFO and PAV treated FHWA Samples

GPC analyses of artificially aged samples of FHWA SBS 64-40, FHWA SBS LG, FHWA PG-70-22m, and FHWA air blown were also carried out to see whether GPC can clearly detect the oxidative changes. The results are presented in Figures 29-32 and in Tables 28-31. All four samples obtained were aged by rolling thin film oven (RTFO) and pressure aging vessel (PAV). RTFO testing is usually done to duplicate aging during manufacturing and conducted by exposing asphalt to air at high temperature (~163-325° F). PAV is done to duplicate long term aging and completed by exposing the binder to air at high temperature and pressure for a short time of period (~20 hours). Figures 29-31 shows the overlaid chromatograms of the FHWA SBS 64-40 FHWA SBS LG, FHWA PG-70-22m and FHWA air blown samples, and aged samples respectively. All four samples clearly show the effect of RTFO and PAV aging.

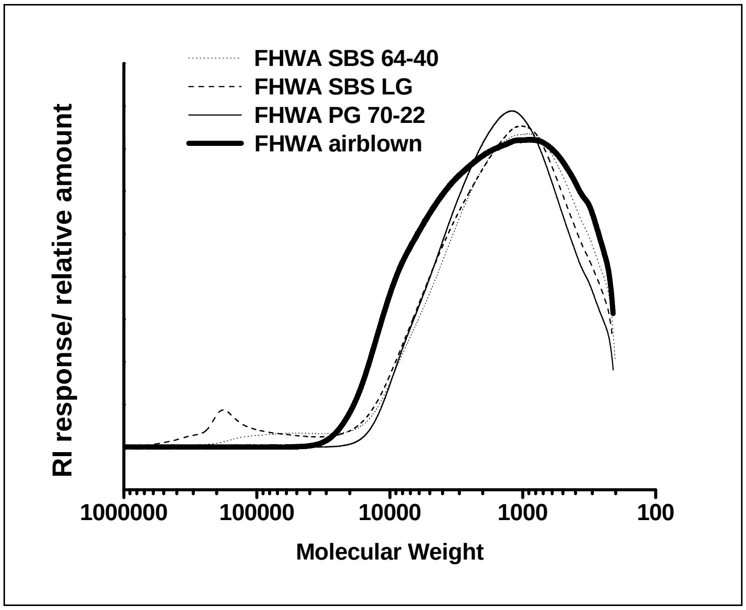

Figure 28

GPC traces of different grades of asphalts from FHWA

Table 27
GPC results of different grades of asphalts from FHWA

FHWA Sample	%VHMW 1M-300K	%HMW 300-45K	%MMW 45-19K	%Asphaltenes 19K-3000	% Maltenes <3000
SBS 64-40	0	1.73	1.25	17.24	79.78
SBS LG	0.77	3.5	1.08	18.68	75.97
PG 70-22m	0	0	0	18.97	81.03
Air Blown	0	0	1	25.83	73.17

The high molecular weight end of the chromatograms increased slightly after RTFO and significantly after PAV aging. This shows that PAV aging produces more changes in the MWD of asphalt. The percentage of polymer, asphaltenes and maltenes content of the analysis are given in Tables 24, 25, 26, and 27, respectively. Results show an increase in polymer and asphaltenes content and a decrease in maltenes content.

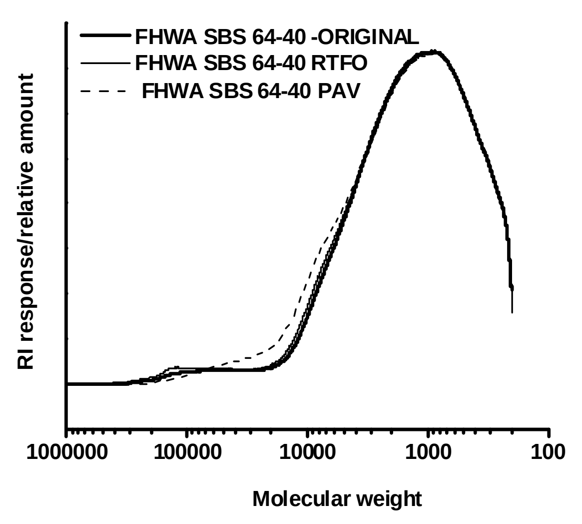

Figure 29
RTFO and PAV treated SBS64-40 FHWA samples

Table 28
GPC results of RTFO and PAV treated SBS64-40 FHWA samples

FHWA SBS 64-40	**1M-300K %**	**300K-45K %**	**45K-19K %**	**TOTAL % polymer 1M-19K**	**Asphaltene % 19K-3000**	**Maltene % <3000**
ORIGINAL	0	1.73	1.25	2.98	17.24	79.78
RTFO	0.09	2.20	1.32	3.61	18.2	78.29
PAV	0	1.4	2.33	3.73	20.11	76.1

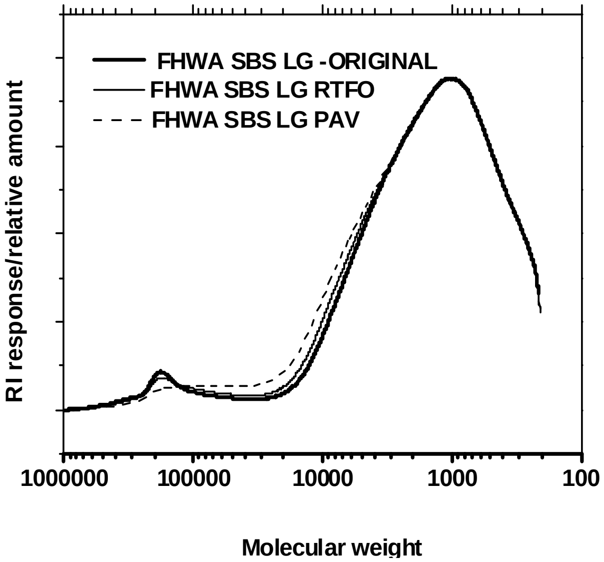

Figure 30
RTFO and PAV treated SBS LG FHWA samples

Table 29
GPC results of RTFO and PAV treated SBS LG FHWA samples

FHWA SBS LG	1000K-300K %	300K-45K %	45K-19K %	TOTAL Polymer %	Asphaltenes %	Maltenes %
ORIGINAL	0.77	3.5	1.08	5.36	18.68	75.97
RTFO	0.70	3.63	1.51	5.84	20.20	73.96
PAV	0.35	3.38	2.27	6.0	20.81	73.19

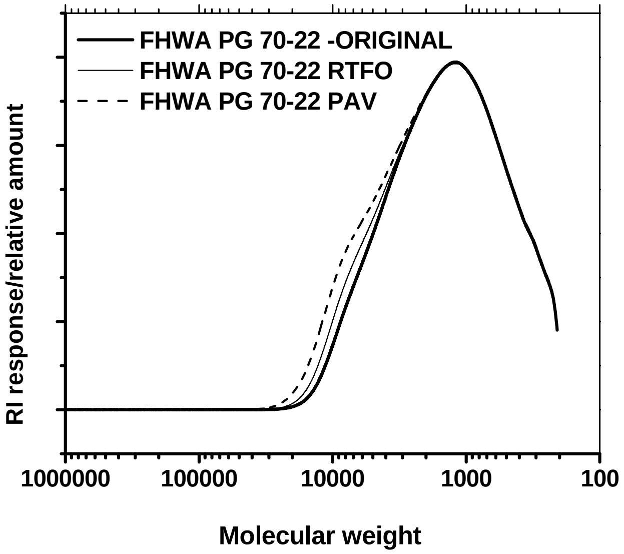

Figure 31
RTFO and PAV treated PG 70-22m FHWA samples

Table 30
GPC results of RTFO and PAV treated PG 70-22m FHWA samples

FHWA PG 70-22m	1000K-300K %	300K-45K %	45K-19K %	TOTAL Polymer %	Asphaltenes %	Maltenes %
ORIGINAL	0	0	0	0	18.97	81.03
RTFO	0	0	0.01	0.01	21.36	78.63
PAV	0	0	0.51	0.51	24.18	75.31

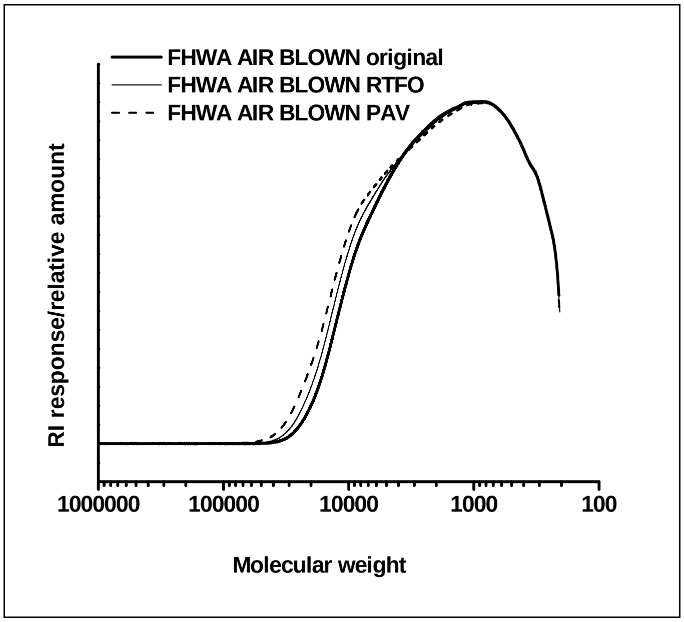

Figure 32
RTFO and PAV treated Air blown FHWA samples

Table 31
GPC results of RTFO and PAV treated air blown FHWA samples

FHWA Air Blown	1000K-300K %	300K-45K %	45K-19K %	Total Polymer %	Asphaltenes %	Maltenes %
ORIGINAL	0	0	1	1	25.83	73.17
RTFO	0	0	1.67	1.67	27.27	71.06
PAV	0	0.12	2.63	2.76	28.14	69.1

GPC Analysis of the THF Extract of Crumb Rubber from Discarded Tires

A commercial crumb rubber (CR) from a discarded tires sample was extracted with THF and the soluble part was subjected to GPC analysis in order to determine the amount and MWD of soluble species, which can be blended with asphalt components during the preparation of CRM binders. Since a powdery HMA (hot mix asphalt) modifier is usually added in the asphalt by contractor together with CR in order to obtain CRM binders, this HMA additive was also dissolved in THF and analyzed by GPC.

It has been determined that 10% of CR was extracted by THF. The corresponding GPC traces indicated that the CR extract contained around 10% soluble polymer which is almost equally distributed in the HMW and MMW regions of the chromatogram, approximately 10% lower molecular weight polymer appearing in the asphaltenes region of the GPC and 80% maltenes (oils).

The HMA modifier was roughly composed of 2.7% MMW polymer, 48.9% asphaltenes and 48.4% maltenes (Table 32). GPC traces of the CR extract are presented together with a PMAC containing 12% polymer in Figure 33a in order to visualize the MW regions in which polymeric species are mainly eluted by the GPC solvent (THF).

The chromatogram of the HMA modifier is shown in Figure 34. It can be seen that the mean MW of the modifier (i.e., the peak of the curve) correspond to the asphaltenes region of the PMAC asphalt (Figure 33). When analyzing a CRM binder, it is therefore necessary to correct the actual content of percentage asphaltenes by subtracting the amount corresponding to added HMA modifier (if known).

Table 32
Results of GPC analysis of 12% PMAC Company A sample, CR extract, and HMA modifier

Sample	1000K - 300K VHMW %	300K – 45K HMW %	45K-19K MMW %	**Total polymer (%)**	**Asphaltenes (%)**	**Maltenes (%)**
PMAC Company A	5.92	5.82	0.67	**12.41**	**16.81**	**70.77**
THF soluble part of crumb rubber	0.34	4.57	5.32	**10.24**	**9.13**	**80.63**
HMA modifier	0.0	0.06	2.61	**2.67**	**48.85**	**48.48**

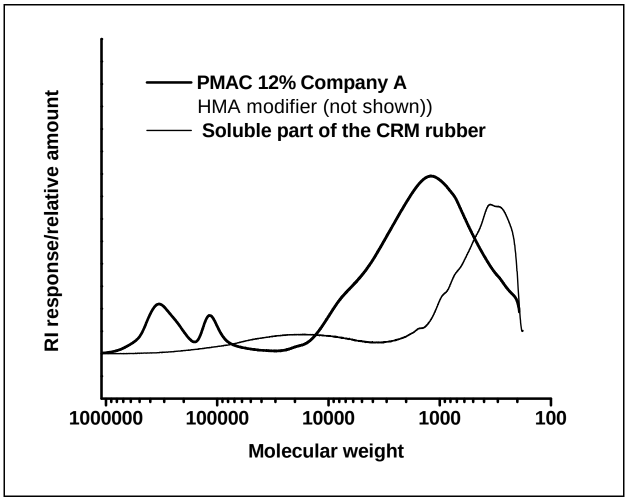

Figure 33
GPC traces of the CR extract and of 12% PMAC (Company A)

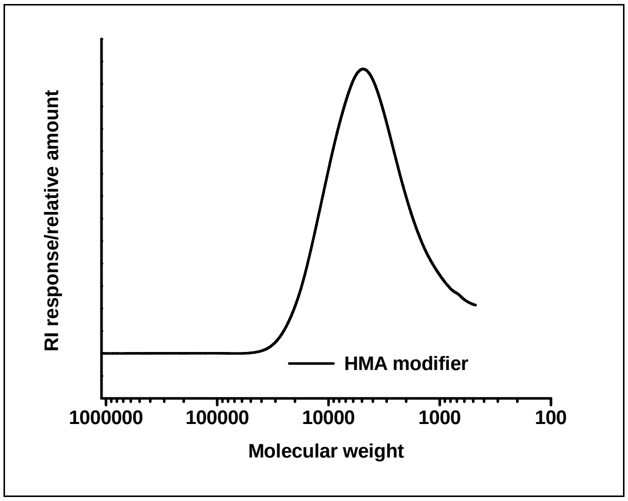

Figure 34
GPC traces of the HMA modifier

CONCLUSIONS

- This project implemented the application of gel permeation chromatography (GPC) at DOTD Materials Laboratory as an analytical tool to ascertain the amounts of polymer modifiers in polymer modified asphalt cements, which are soluble in eluting GPC solvents. To this aim, a robust state-of-the art GPC system was installed in a DOTD Materials Laboratory room dedicated solely to preparation and analysis of samples received from Louisiana suppliers of paving asphalt materials. An effective asphalt binder extraction method to extract asphalt from CRM modified binder, without affecting the binder properties was developed.

- A simple GPC procedure for determining the composition of asphalt binders based upon the molecular size of the components was developed for routine characterization.

- The project addressed quantification of both GPC solvent soluble and insoluble crumb rubber present in crumb rubber modified binders. A procedure to define the percent amounts GPC solvent insoluble crumb rubber present in CRM binders was developed.

- The gel permeation chromatography technique was applied to over 250 samples from 10 commercial sources supplying asphalt paving materials to Louisiana.

- From the GPC data of asphalt binders collected at the DOTD Materials Laboratory and presented in this report it has been found that suppliers are using different types of SBS polymer at different percentages. In order to meet the requirements for a PG 70-22m they add at least 1 wt. % polymer, while to achieve PG 76-22m a minimum of 2 wt % polymer is necessary to be introduced.

- Using the GPC technique, the extent of oxidative RTFO and PAV aging was assessed in terms of polymer, asphaltenes, and maltenes content for a series of sampled binders from FHWA including PMAC and air blown asphalts.

- The project illustrated the forensic application of GPC regarding paving problems encountered in the field.

- An AASHTO Standard test method for the Quantification of polymer content in PMAC (polymer modified asphalt cement) by High Performance Size Exclusion Chromatography (HPSEC) has been proposed.

RECOMMENDATIONS

A simple GPC procedure for determining the composition of asphalt binders based upon the molecular size of the components was developed for routine characterization. The GPC test should be implemented for all asphalt binders supplied to LADOTD, to ascertain the amounts of polymer modifiers in polymer modified asphalt cements. From the GPC data of asphalt binders collected at the DOTD Materials Laboratory and presented in this report, it has been found that suppliers are using different types of SBS polymer at different percentages. The data suggest that in order to meet the requirements for a PG 70-22m at least 1 wt. % polymer should be present, while to achieve PG 76-22m a minimum of 2 wt % polymers is required. The minimum polymer content should be incorporated into the standards for binder acceptance. An AASHTO standard test method for the quantification of polymer content in PMAC by High Performance Size Exclusion Chromatography (HPSEC) is submitted for approval.

A gravimetric procedure to determine the percentage amounts solvent insoluble crumb rubber present in CRM binders was developed. The soluble components of the CRM binder were extracted using a blend of toluene-ethanol (85:15 volumetric ratios). This technique should be employed for quality assurance of CRM binders.

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	Department of Transportation
DRI	Differential Refractive Index
DSR	Dynamic Shear Rheometer
δ	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
Jc	Critical Strain Energy
kJ	Kilo Joule
LALS	Low Angle Light Scattering
LMS	Large Molecular Size
LTRC	Louisiana Department of Transportation and Development
µ	Micro
M	Million
min.	Minute
mL	Milliliter
MMS	Medium Molecular Size
MMW	Medium Molecular Weight
mv	Mill volt
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	Styrene-Butadiene-Styrene Triblock 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

Standard test method for the

Quantification of polymer content in polymer modified asphalt cement (PMAC) by High Performance Size Exclusion Chromatography (HPSEC).

AASHTO Designation: XXXX

Standard test method for the

Quantification of polymer content in polymer modified asphalt cement (PMAC) by High Performance Size Exclusion Chromatography (HPSEC).

AASHTO Designation : XXXX

1. SCOPE

This test method covers the quantification of high molecular weight polymer blended with asphalt in a polymer modified asphalt (PMAC) using a high performance Size Exclusion chromatography. This technique is not absolute; and depends on the calibration curve prepared using polystyrene standards of known molecular weight. The method is applicable to PMAC samples which contain polymers which are soluble in tetrahydrofuran solvent. The analysis was done at 40°C. The molecular weights of the components of PMAC should have elution time falling within the range polystyrene standards.

Note 1 –Size exclusion chromatography (SEC) is often used as an alternative name for gel permeation chromatography.

Note 2 - HPSEC differ from traditional SEC in that HPSEC uses columns with about ten times the number of theoretical plates per meter (see terminology D883 and ASTM standard D-3016). Features and requirements of an HPSEC are given in ASTM D 5296-05.

Note 3 – One general method is summarized here using HPSEC. Alternatively traditional high temperature SEC instrument can also be used to obtain such quantification by the proper selections of columns and standards.

2. REFERENCED DOCUMENTS

ASTM standards

D5296 -05	Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography.
D6474	Standard Test Method for. Determining Molecular Weight Distribution and Molecular Weight Averages of Polyolefins by High Temperature Gel Permeation Chromatography.
D883	Terminology relating to plastics
D3016	Practice for Use of Liquid Exclusion Chromatography terms and Relationships

3. TERMINOLOGY

For definitions of size exclusion chromatography terms which are not given, see ASTM D3016

GPC –Gel Permeation Chromatography (a chromatographic method of separation of molecules based on their size in a solution of a particular solvent). GPC is also known as SEC (Size Exclusion Chromatography).

RI – Differential Refractive Index detector: This detector measures the change in refractive index of the solution (with respect to the solvent) which is eluting from the columns. The RI is directly related to the concentration of the component in the solution passing through the detector.

Retention time: The time it takes for a particular component in the solution to pass from the injector through the columns to the detector.

Chromatogram – A plot of elution time vs. refractive index detector response or, a plot of molecular weight or log molecular weight vs. refractive index detector response. In the latter case, the retention volumes are converted in to molecular weight using calibration curve prepared using narrow molecular weight polystyrene standards.

SBS - A polystyrene-b-polybutadiene-b-polystyrene block copolymer employed as a polymer additive.

MWD – Molecular weight distribution, represents the relative weight fraction of different molecular weight(size) molecules that comprise a particular sample.

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4. SUMMARY OF THE METHOD:

1. In this method, a dilute solution of asphalt or polymer modified asphalt (PMAC) sample dissolved in tetrahedron (THF) solvent is injected into a THF liquid mobile phase. The mobile phase transports the sample into and through a set of chromatography columns packed with a rigid or semi rigid porous substrate that separates the molecules according to their size (hydrodynamic volume) in the solution. A detector (Difference refractive Index and UV (optional) monitors the concentration of eluates as a function of elution time (or elution volume). Upon emerging from the column(s), the weight fraction of size-separated molecules are detected and their elution times (volumes) vs. the detector signal are recorded. A calibration curve which relates the elution time of samples with known molecular weights is used to convert elution times (volumes) to apparent molecular weights.

The chromatograph is analyzed according to the molecular weight of the components in the mixture. High molecular weight polymers elute at lower retention times than the asphalt components.. Using the GPC software, the relative area of the components with molecular weights higher than 19,000 Daltons is compared to the total area of all the components. The ratio of the component area the total area is assumed to be equivalent to the weight fraction of polymer present in PMAC.

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5. MATERIALS AND REAGENTS

3. Tetrahydrofuran. (HPLC grade)

4. 2,6-Di-tert-butyl-4-methylphenol (Butylated hydroxytoluene **(**BHT)), peroxide inhibitor.

(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 (1g BHT is normally added in a 4L bottle of THF))

5. Calibration Standards: Unimodal, narrow molecular weight distribution (MWD) polystyrene Standards of known molecular weights are preferred for calibration. Tosoh Bioscience's PStQuick B, PStQuick E and PStQuick F are ready to use standards which are cocktails of two or more narrow MWD polystyrene (PS) standards.

    3.1 PStQuick B contains PS with M.W. 5480000, 706000, 96400, 10200, and 1000.

    3.2 PStQuick E contains PS with M.W 355000, 37900, 5970, and 1000.

    3.3 PstQuick F contains PS with M.W 190000, 18100, 2500, and 500**.**

One can use polystyrene standards available from other suppliers which cover the range of polymer and asphalt molecular weight. Selection of minimum of three standards per decade in molecular weight across the effective molecular weight range of the column set is recommended (D6579).

6. APPARATUS

High-performance Size exclusion Chromatography (HPSEC), EcoSEC high performance GPC system (HLC-8320GPC)system from Tosoh Corporation or equivalent. Typical HPSEC components and performance requirements are thoroughly explained in ASTM D5296.

6.1	High-performance Size exclusion Chromatography (HPSEC), EcoSEC high performance GPC system (HLC-8320GPC)system from Tosoh Corporation or an equivalent SEC which can perform from 10 to 60°C. Typical HPSEC components and performance requirements are thoroughly explained in ASTM D5296.
6.2 **6.2.1** **6.2.2** **6.2.3** **6.2.4** **6.2.5** **6.2.6**	Other HPGPC system hardware- - HPLC pump for isocratic solvent or gradient delivery. **Note 1**- Isocratic pump is for a single solvent and here tetrahydrofuran is the solvent - Mobile phase Guard column Guard SuperHz-2 Tosoh or equivalent . - GPC columns used for separation 1. TSK gel, Super Hz 4000, 6.0 mm ID x 15 cm, pore size 200Å, polystyrene MW range exclusion 4×10^5 (1 column) 2. TSK gel, Super Hz 3000, 6.0 mm ID x 15 cm, pore size 75Å, polystyrene MW range exclusion 6×10^4 (2 columns) 3. TSK gel, Super Hz 2500, 6.0 mm ID x 15 cm, pore size 30Å, polystyrene MW range exclusion 2×10^4 (1 column) High Performance GPC System Auto sampler (100 sample capacity, 1 to 1500 µl in volume per injection)- EcoSEC Tosoh Corporation model HLC-8320GPC or equivalent **Note 2-** In the absence of auto sampler, a manual injection system can be used. Differential Refractive index detector (from TOSOH) – Bryce-type double path or double flow or an equivalent.

	Optional detector UV (UV-8320 from TOSOH) working range (195-350 nm) or equivalent **Note 3 -** to monitor the UV absorbing species of asphalt.
6.2.7	Column Oven – temperature range fro 10 to 60° C or equivalent.
6.3	Glass Scintillation vials (20 mL) with cone screw caps, Wheaton* Glass 20mL scintillation Vials with Poly-seal Cone Cap Liner, Wheaton Science Products Inc. No 986586 or equivalent
6.4	Glass Burette 25 mL
6.5	3mL Disposable Syringes : AirTite* Norm-Ject* with Luer-Lok^{TM} fitting, Air Tite Products Co No.:AL3, (Fisher Scientific catalog number :14-817-27) or equivalent
6.6	Needles- Gauge: 18; O.D.: 1.24mm; Length: 38mm, BD PrecisionGlide* BD Medical No.:305196 (Fisher Scientific catalog number 14-826-5D) or equivalent .
6.7	Pipette bulb 2mL (Fisher Scientific No**:** 15-000-506) or equivalent
6.8	Syringe Filters with Luer-Lok* Inlet, PTFE; Diameter: 13mm; Porosity: 0.45um **(**Restek Catalog No : 06-802-785, Fisher Scientific catalog No 06-802-785) or equivalent
6.9	2 mL Autosampler; Clear Glass with Write-on Spot; Screw-top without cap, (Krackeler Scientific Agilent No.:5182-0715 (Fisher Scientific catalog No.HP 51820715N)) or equivalent
6.10	Screw Caps for the auto sampler with Septa, (Krackeler Scientific Agilent No. 51820717N) Fisher Scientific catalog No. HP 51820717N)) or equivalent.
6.11	Analytical Balance for weighting

7. PREPARATION OF SOLUTIONS

7.1 Preparation of Polystyrene Standards:

The typical concentration range for polystyrene standards is from 0.2 to 1 mg/mL. Weigh appropriate amount of standard polymer into a suitable vial or standard flask and add appropriate amount of THF, close the screw caps and allowed to stand overnight without shaking. Prior to analysis the vial should shaken gently. Mixture of two or more polystyrene standards with different molecular weight may be prepared in the same flask.

Tosoh PStQuick series (B, E and F) which come pre-weighed in glass vials. Each vial contains mixture different narrow molecular weight standards of polystyrenes. Add 1 mL of THF in these vials, and close the screw caps and allowed to stand overnight without shaking. Prior to analysis the vial should shaken gently. These standards provide a wide range of molecular weight standards which extends from very high molecular weight to very low molecular weight. Hence it is ideal for the analysis of a mixture of asphalt (low molecular weight) and polymer (high molecular weight). The following standard mixtures were employed:

3.1 PStQuick B (MW= 5480000, 706000, 96400, 10200, 1000)
3.2 PStQuick E (MW= 355000, 37900, 5970, 1000)
3.3 PstQuick F (MW= 190000, 18100, 2500, 500**)**

7.2 Preparation of asphalt samples:

Asphalt samples were dissolved in THF concentration of either 1% or 0.25 % (All samples were prepared on the previous day and filtered on the day of analysis using 0.45 micron Teflon filters.)

7.3 Preparation of 1% solution: Using an analytical balance weigh ~100mg (± 0.5 mg) of asphalt in to a 10mL volumetric flask. Add THF to 10 mL and close the flask tightly. After mixing it gently, keep the flask overnight for the complete dissolution. Prior to filtration, mix the contents again. Alternatively, ~100mg (± 0.5 mg) of asphalt can be weighed into a 20 mL scintillation vial and exactly 10 mL THF can be added to the vial using a burette. Seal with a screw cap, mix and keep overnight for the complete dissolution. Prior to filtration, mix the contents again.

7.4 Preparation of 0.25% solution: Using an analytical balance weigh ~25mg (± 0.5 mg) of asphalt and prepare a solution as described above.

7.5 Solution filtration: A 5 mL syringe, 0.45um PTFE filter and disposable glass pipette with rubber bulb are required for this. First remove the plunger of the syringe attached to a 0.45um PTFE filter via a Luer-Lok. Carefully add 2.3 mL of asphalt solution into the syringe using a disposable pipette. Insert the plunger back into the open syringe, while carefully inserting the filter outlet into an auto sampler vial. Push the plunger slowly so that filtered solution collects in the vial. Cap and label the vial.

8. GPC PROCEDURE

8.1 The procedure is given for the TOSOH GPC system. For other systems follow the instruction manual of the system and set the conditions according. In TOSOH GPC system (HLC-8320GPC), the operation of the instrument and setting of parameters are performed in the instrument control screen of the acquisition control program. To start analysis, start the power button at the top of the acquisition control program screen and click on warm up screen. Click the instrument parameter from the operating menu and select the desired parameters for analysis. The following settings can be employed for 15 cm-1 column sets: solvent flow rate, 0.35 mL/min, reference flow ratio, equal, column and pump oven temperature, 40°C. Set the RI detector balance value (mV) to 30.000 and response (sec) to 0.5. Set the UV detector wavelength (nm) to 254 (if needed) and balance value (nm) to 30.000, and response (sec) to 0.5. Click the warm up tab to bring the warm up screen. Allow 30 min for the instrument to complete the warming up process and assure that the RI baseline is stable.

All data collected in the present report have been acquired using the best combination of columns for GPC analysis at 40°C viz., the four column set described above (Materials section, #9). Using sample concentrations of 0.25% or 1.00% and eluting at 0.35 mL/min (if not stated otherwise), the total time for a sample analysis was less than 60 minutes.

9. Calibration

First, calibrate the instrument using freshly prepared calibration standard solutions (PStquick B, E & F or equivalent) in the given vials (2 mL), as explained in the previous section. Load the auto sampler by pressing the rack eject/insert key in the control section of the instrument. Place the solution vials on to the auto sampler. Remount the sample rack on the instrument by pressing rack eject/insert key. Click on the sample queue screen on the acquisition control program; enter the sample queue name, name of the samples and various settings for the solutions loaded in the auto sampler. Follow the quick reference manual for the instructions. For calibration standards, total time for analysis is 30 minute, injection volume 10 µL, two repeat, 254 nm as UV wavelength. After entering these values, check the error and start analysis. Use the quick reference manual of High-performance GPC system HLC-8320GPC EcoSEC-WorkStation for creating method, calibration, analysis conditions and saving of the data.

The chromatograms of the PST quick B, E and F are shown in Figure 1, 2 and 3. Open the analysis program and using the GPC software, do a base line correction and peak edition to obtain a retention time for each peak. In the calibration method screen of the software, enter the retention values (peak maximum) and corresponding molecular weights of the standards in the three solutions in a table as instructed in the instrument software (shown in table 1). The combined calibration data is shown in Figure 4. The software will create a calibration curve of retention time vs. log molecular weight as shown in Figure 5. This will be used for the analysis of asphalt samples.

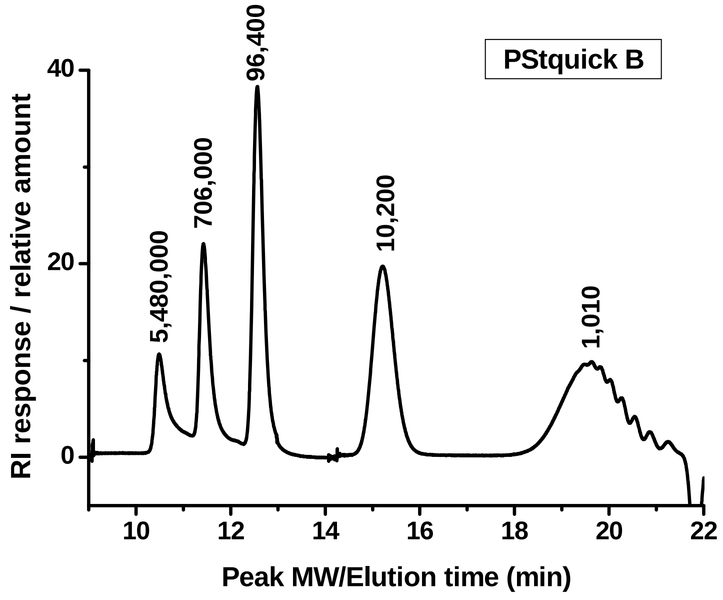

Figure 1.

GPC chromatogram of PStQuick B in THF, 0.35ml/minute, 40°C.

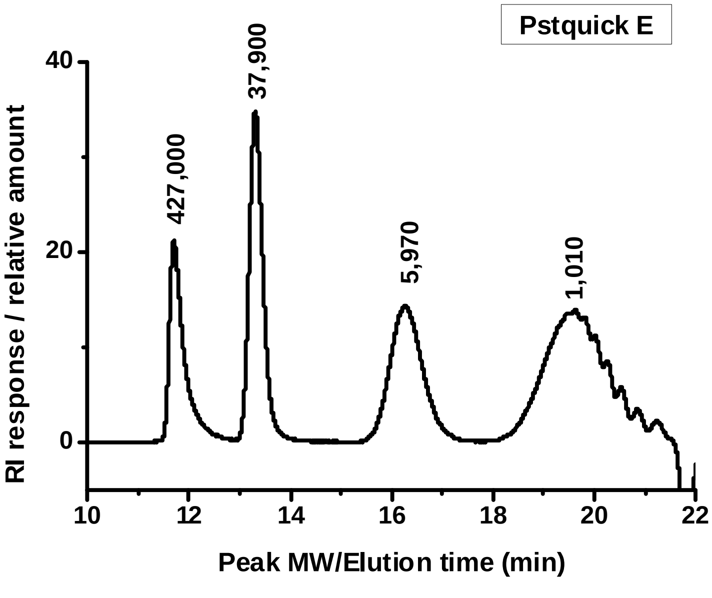

Figure 2.

GPC chromatogram of PStQuick E in THF, 0.35ml/minute, 40°C

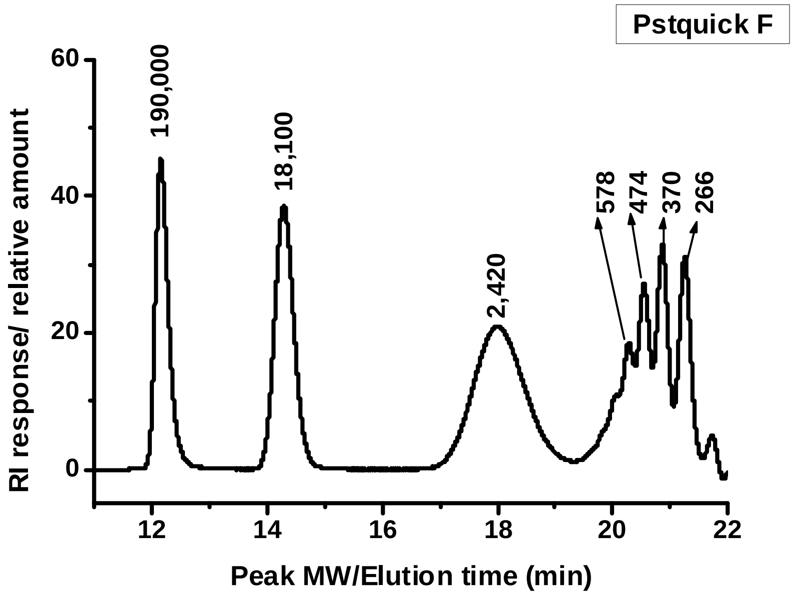

Figure 3.

GPC chromatogram of PStQuick F in THF, 0.35ml/minute, 40°C

Table 1.

Example of GPC calibration data obtained using Pstquick B, E and F series

Retention time	Molecular weight (Daltons)	Log molecular weight
10.487	5480000	6.73878
11.427	706000	5.8488
11.695	427000	5.63043
12.147	190000	5.27875
12.565	96400	4.98408
13.308	37900	4.57864
14.282	18100	4.25768
15.215	10200	4.0086
16.262	5970	3.77597
17.995	2420	3.38382
19.623	1010	3.00432

19.637	1010	3.00432
20.278	578	2.76193
20.543	474	2.67578
20.863	370	2.5682
21.252	266	2.42488

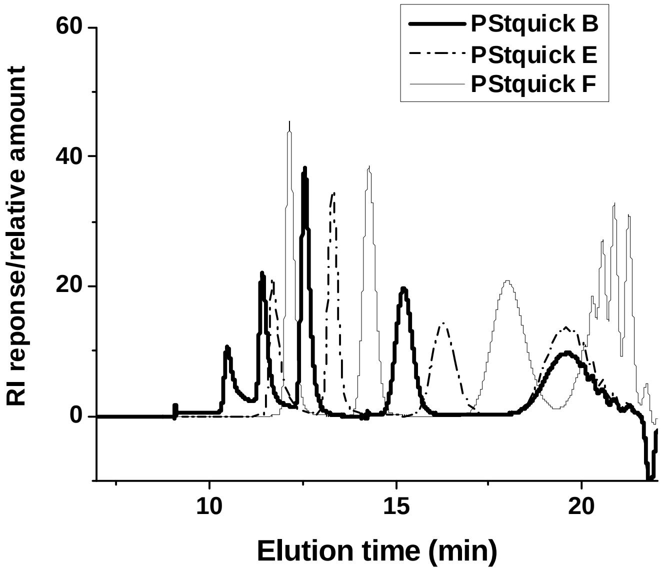

Figure 4.

Combined chromatograms of polystyrene standards

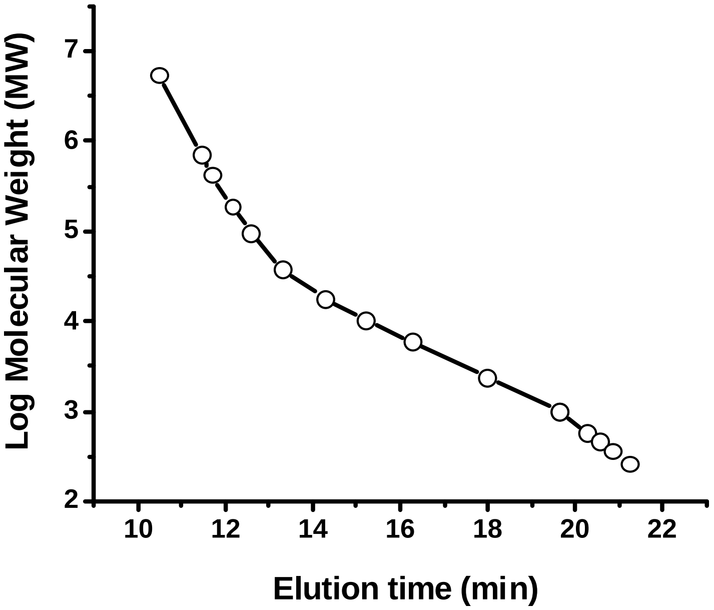

Figure 5.

Calibration curve prepared from elution time of polystyrene standards

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10. INSTRUCTIONS FOR ANALYSIS OF ASPHALT AND RELATED SAMPLES

Prepare a solution as explained in an earlier section. Using 15 cm columns a 0.25% wt/volume solution gives good detector response which has magnitude comparable to the PS standards. If 30 cm columns are used, the solution concentration should be raised to 1.0% wt/volume. Filter the solution to 2 ml vials suitable for use in auto sampler. Load the samples and use the same settings as for the calibration except the time of analysis. For asphalt analysis, 30 minutes is satisfactory but 60 minutes assures that the column is completely flushed of all the components of asphalt.

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11. RESULTS AND CALCULATIONS

11.1 Typical chromatogram of the 1% solution of the reference asphalt (company A) in THF solvent is shown in Figure 6. This is an example of asphalt which has no polymer added to it. It shows the plot of 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. Figure 7 shows the GPC chromatogram of polymer modified asphalt (PMAC). This sample has 12% polymer added. At a lower retention time (11 to 14 minutes), the polymer peaks appear and they are clearly distinguishable from the asphalt envelope.

11.2 After the analysis, the chromatograms are base line corrected and peak edited using the GPC software. The RI data is converted tothe corresponding molecular weights using the calibration curve obtained using the polystyrene standards.

11.3 A superimposed S GPC traces of neat asphalt and of its derived PMAC are shown in Figure 8. A clear separation of polymer peaks from asphalt peaks can be seen. The polymer, having a higher molecular weight compared to that of the asphalt comes in the range of MW of 1,000,000 to 19,000 Daltons. This difference in molecular weight makes it easy to quantify the amount of polymer in a blend of polymer and asphalt or in polymer modified asphalt cement (PMAC) materials. The area from 19,000 to low molecular weight end can be considered as total asphalt present (viz., containing only asphaltenes and maltenes).

11.4 Identify the retention time corresponding to the 19,000 molecular weight. Then the polymer content of the asphalt can be determined by the integration of the total area.
% Polymer Modifier = Area of the polymer peak / (Area of polymer peak + Area of asphalt peak).

11.4.1 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, which should be omitted during the area calculations.

11.5 The amount of polymer in the asphalt calculated from Figure 7 was 12.41%.

11.6 Comparison of 1% and 0.25 % of a PMAC sample in THF is shown in Figure 9. There is a slight effect of concentration on the high molecular weight portion of the curve.. At lower concentrations the solution viscosity is minimized and the tendency for peak spreading is reduced. The total polymer content obtained for 1% and 0.25% THF solution of PMAC in this case were 2.27 % and 2.53% respectively.

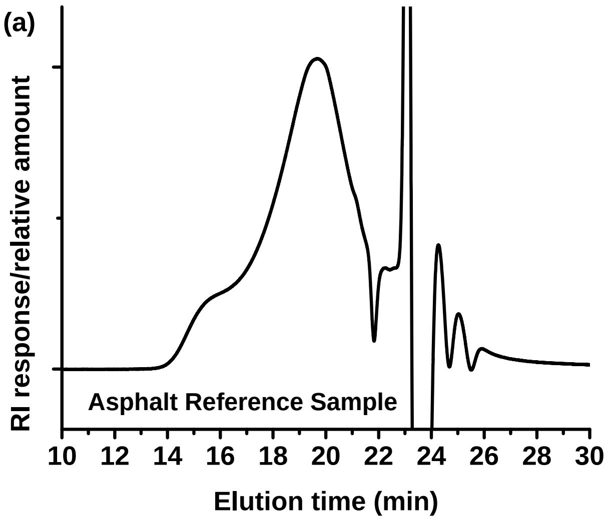

Figure 6.

Typical chromatogram of Asphalt

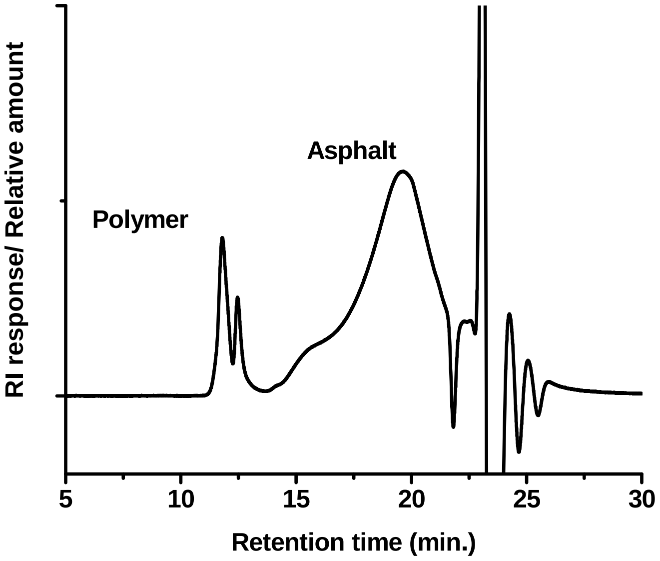

Figure 7

Typical chromatogram of Polymer modified asphalt (12% polymer)

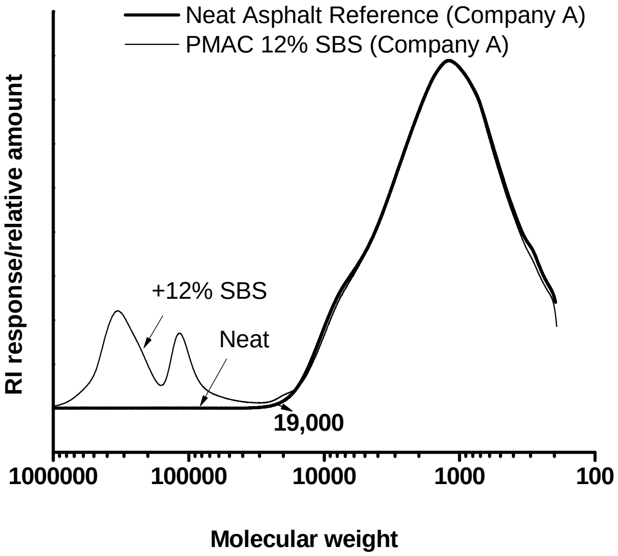

Figure 8.

Superimposed GPC traces of neat asphalt and of its derived PMAC (X-axis –retention time is converted to molecular weight)

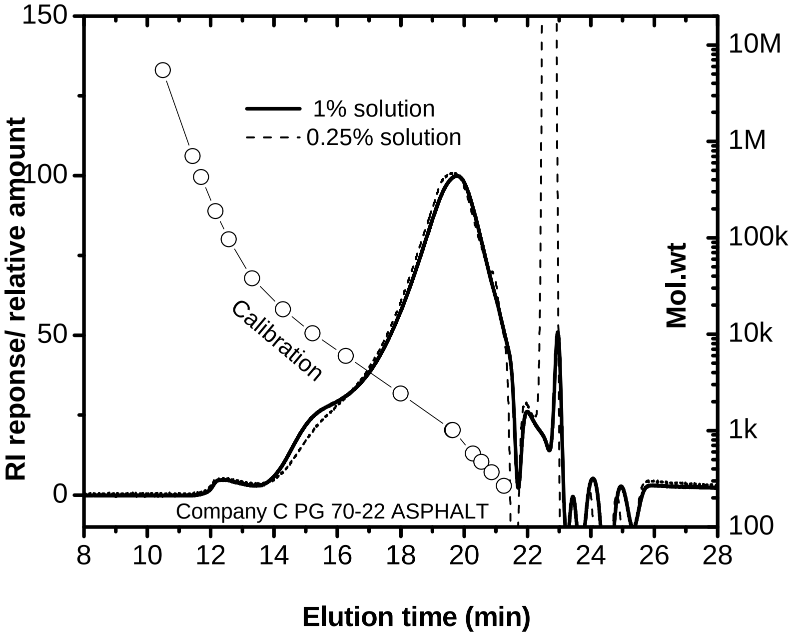

Figure 9.

GPC traces of Polymer modifier asphalt materials at 1% and 0.25 sample concentrations in THF

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12. REPORT

12.1 Report the following in formations

12.1.1 GPC model and number

12.1.2 Details of the column used with packing type, dimensions and manufacturer.

12.1.3 Column temperature

12.1.4 Solvent (THF) and the amount of BHT added

12.1.5 Solvent flow rate (mL/min)

12.1.6 Detector type and model number

12.1.7 Injection volume, µL,

12.1.8 Polymer sample solution concentration

12.1.9 Polymer used for Calibration

12.2 Percentage of polymer detected.