



# TECHSUMMARY *January 2010*

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## A Comparative Analysis Of Modified Binders: Original Asphalts And Materials Extracted From Existing Pavements

### INTRODUCTION

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. A separation of the components is possible using gel permeation chromatography (GPC), which 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. GPC methodology was applied to follow the processing and paving sequences and to determine the changes in the mix during its lifetime. The research involved quantitatively assessing (1) the amount of the polymeric species in a polymer modified asphalt cement (PMAC) as received from a supplier, including changes imparted by the addition of recycled asphalt pavement (RAP) to the mix; (2) the amount of the polymeric modifier in the liquid extracted from cores taken from a new road paved with the same PMAC as that received from a supplier; and (3) the extent of on-the-road degradation of the polymeric species by oxidative aging for periods up to 20 months. The research was extended to evaluate mixes containing a crumb rubber modifier (CRM), which is practically insoluble in GPC solvents.

### OBJECTIVE

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

### SCOPE

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

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## METHODOLOGY

Asphalt and polymer modified asphalt materials were obtained directly from refineries. A group of 29 asphalt binder samples from five different refineries were analyzed along with binder specimens that were extracted from samples collected at the contractor plant after the drum mixing process. A hot toluene extraction method was used to isolate asphalt binder from all mix samples. Asphalt binder specimens were extracted from RAP mixtures used by the contractors when the samples were available. Asphalt binder specimens were also extracted from hot mix asphalt (HMA) after transported to the job site. Binder specimens were extracted from road cores with the following ages: new, 6 months, and 1 year. Samples of five commonly used poly[styrene-*b*-butadiene-*b*-styrene (SBS)] were obtained from the refineries and analyzed by GPC. Since GPC requires no more than 0.3 g asphalt, an alternate extraction procedure for small scale samples was employed. A gravimetric procedure for CRM analysis was developed.

Seven different sets of columns with different porosities and two eluting solvents [tetrahydrofuran (THF) and toluene] were evaluated to determine the most distinct separation of asphalt components. The researchers ascertained that eluting with THF through a four column set with porosities of 500, 103, 104 Å, and a linear mixed porosities was the best combination of columns for GPC analysis at room temperature.

Three asphalt binders were selected for laboratory characterization using DSC and DMA. The presence of crystalline species (considered mostly as paraffinic maltenes) was determined using DSC, and the binder glass transition's temperature (T<sub>g</sub>) was determined by DMA.

## CONCLUSIONS

This research demonstrated the application of GPC as an analytical tool to ascertain the amounts of polymer modifiers in polymer modified asphalt cements, which are soluble in eluting GPC solvents. Adding RAP during the mixing process increases the asphaltene content with a corresponding decrease in the maltenes content. An assessment of the extent of oxidative aging of modified asphalt binders during the paving process confirmed minimal changes during the paving process. Field aging of mixes containing RAP was slower than that predicted by the rolling thin film oven

(RTFO); aging suggested that an addition of 20 wt% RAP was beneficial. Although suppliers are using different types of SBS at different percentages to meet the requirements for a PG 70-22, the authors observed that 1 wt% up to 1.98 wt% polymer was generally added. To achieve PG 76-22, the authors observed that a minimum of 2 wt% polymer was added. The GPC test method can identify the type of polymer used as well as the percentages of polymer and asphaltenes present.

The content of crystallizable species of selected asphalt binders determined by DSC is reported together with the binder T<sub>g</sub>s determined by DMA. DMA results showed that asphalt binders characterized by high stiffness and poor extensibility at low temperatures have a higher T<sub>g</sub> than that of low stiffness binders. A method for quantification of insoluble crumb rubber modifier present in crumb rubber modified binders was developed.

The application of the technique to forensic studies of problem issues including high voids content and bleeding was demonstrated.

## RECOMMENDATIONS

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