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Implementation of GPC Characterization of Asphalt Binders at Louisiana Materials Laboratory

INTRODUCTION

Asphalt is a mixture of a wide variety of chemical compounds that include aliphatic hydrocarbons and highly fused aromatic ring systems. They are classified as asphaltenes (medium 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 SBS (polystyrene-b-polybutadiene-b-polystyrene, a block copolymer) and SBR (polystyrene-polybutadiene rubber) 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 gel permeation chromatography (GPC). As shown previously, the polymer and asphalt components of polymer-modified asphalt cements can be separated completely using gel permeation chromatography. 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.

OBJECTIVE

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 crumb rubber-modified (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 (RTFO and PAV), forensic analysis of pavement failures, and analysis of asphalt emulsions.

SCOPE

The project was sub-divided into two phases including (I) the purchasing, installating and calibrating of a Tosoh EcoSEC high performance GPC system (HLC-8320GPC), shown below, at the DOTD Materials Laboratory and conducting tutorials regarding detailed procedures for conducting binder analysis to determine the percentage of polymer content in polymer modified binders; and (II) developing more efficient extraction processes capable of recovering asphalt from CRM asphalt cements. A catalog containing

Tosoh EcoSEC high performance GPC system (HLC-8320GPC)

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PRINCIPAL INVESTIGATOR:

William H. Daly, Ph.D.
Ioan Negulescu, Ph.D.

LTRC CONTACT:

Bill King, P.E.
225-767-9129

FUNDING:

SPR: TT-Fed/TT-Reg

Louisiana Transportation Research Center

4101 Gourrier Ave
Baton Rouge, LA 70808-4443

www.ltrc.lsu.edu

over 200 GPC data has been compiled 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 solutions. 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. The use of micro columns is recommended to reduce sample size and total elution volume to conserve solvent. The size-separated molecules are detected using differential refractive index that correlates to their concentration. Through calibration with monodisperse polystyrene standards, elution volumes are converted to molecular weights and various molecular weight parameters for the samples calculated from the molecular weight-concentration data (ASTM D6474). Tetrahydrofuran (THF) solutions of binder samples are injected into 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 weights. 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.

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 was extracted using either a blend of toluene-ethanol (85:15 volumetric ratio) or bromopropane at room or moderate temperatures. Both of them yielded similar crumb rubber residues that correlated with known crumb rubber contents in test mixes. Thus, the use of the less expensive toluene ethanol mixture is recommended.

CONCLUSIONS AND RECOMMENDATIONS

This project implemented the routine application of GPC at the DOTD Materials Laboratory as an analytical tool to ascertain the amounts of polymer modifiers in polymer-modified asphalt cements that 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 the preparation and analysis of samples received from Louisiana suppliers of paving asphalt materials. An effective process capable of recovering asphalt from CRM asphalt cements using a solvent mixture of toluene and ethanol (85:15 volumetric ratio) without affecting the binder properties was also developed. 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 polymers 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 % polymer is required.

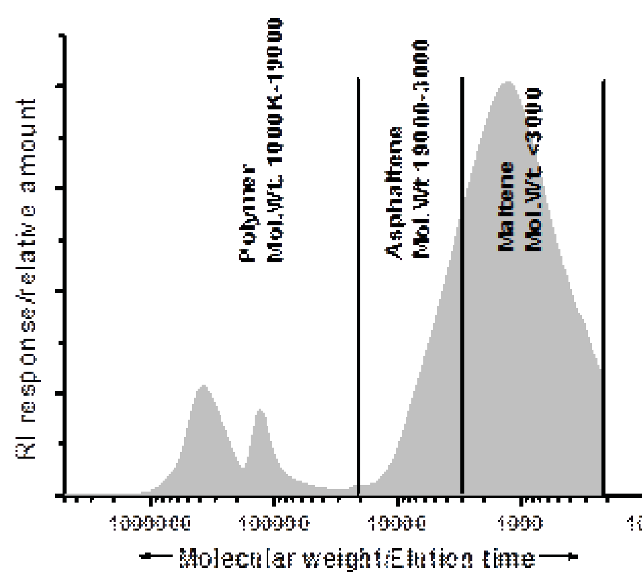

Figure 1
Molecular weight zones assigned in PMAC GPC Chromatogram