TOSOH

Application Note

ANALYSIS OF ASPHALT BINDERS USING GEL PERMEATION CHROMATOGRAPHY

INTRODUCTION

Asphalt is a mixture of a wide variety of chemical compounds that include aliphatic hydrocarbons and highly fused aromatic ring systems. The components of asphalts are classified into two categories based on their molar mass. Medium molar mass asphalt components are classified as asphaltenes and low molar mass components are classified as maltenes. To improve the final properties of asphalts a high molar mass polymer known as the asphalt binder can also be added to the mixture of asphaltenes and maltenes, resulting in the formation of polymer-modified asphalt cements (PMACs). PMACs can be made from polystyrene-b-polybutadiene-b-polystyrene (SBS) and polystyrene-polybutadiene rubber (SBR). The addition of these types of polymers results in polymer-modified asphalt binders that are regarded as a true solution in which the polymer is homogeneously blended with the components of the base asphalt cement.

Polymer-modified asphalt binders are of great importance as unmodified, or neat, asphalt is sensitive to high and low temperatures when used in roads. Thus, during the summer, the asphalt softens, while during winter it becomes more rigid and tends to crack. These changes cause rutting and deformation of the asphalt hindering its ability to perform as it was designed. The addition of the high molar mass polymers to the asphalts ensures good performance as they make the asphalt more elastic over a larger temperature domain. Asphalts, just like other materials containing polymeric materials, must be characterized to determine their end-use properties or environments. One method that is ideal for the characterization of the three species of PMACs: asphaltenes, maltenes and polymer, is gel permeation chromatography (GPC).

Typical polymer asphalt GPC chromatograms have a clear separation of polymer from asphalt in the elution sequence being that the polymer has a higher molar mass than that of the other asphalt components. This difference in molar mass obtained via GPC also makes it easy to quantify the amount of polymer in a blend of polymer and asphalt or in PMAC materials. Here, we have utilized the EcoSEC GPC System to achieve three different objectives: (1) to separate the three species of PMACs, asphaltenes, maltenes and polymer molecules from one another and to characterize the molar mass averages based on polystyrene standards, (2) to compare the molar mass distributions and GPC elution profile PMACs created from polymer molecules from different suppliers, and (3) to analyze a large number of asphalts and correlating relative concentration values with binder properties to give a better understanding in the selection/modification of asphalt with better performance.

EXPERIMENTAL

Sample analysis was performed on a system consisting of an EcoSEC GPC System equipped with a RI detector. Samples were filtered through a 0.45 µm PTFE filter and injected onto a column bank consisting of a 6.0 mm ID × 15 cm, 3 µm TSKgel® SuperHZ4000 (exclusion limit 4×10^5 g/mol, PN 0019312), two 6.0 mm ID x 15 cm, 3 µm particle size TSKgel SuperHZ3000 (exclusion limit 6×10^4 g/mol, PN 0019311) and a 6.0 mm ID x 15 cm, 3 µm TSKgel SuperHZ2500 (exclusion limit 2×10^4 g/mol, PN 0019304). The mobile phase and eluent was THF stabilized with butylated hydroxytoluene (BHT) as a peroxide inhibitor at a flow rate of 0.35 mL/min. Detector, pump oven, and column oven were maintained at 40 °C.

For all chromatographic determinations, results are averages of two injections. The molar mass and molar mass distribution of the asphalt samples was determined based on a polystyrene calibration curve. The calibration curve was created for the RI at 40 °C using PSt Quick Kits B, E, and F, ranging in molar mass from 266 to 5.5×10^6 g/mol. Calibration curve data for 0.35 mL/min was fitted with a cubic function and error values were less than 5%.

RESULTS AND DISCUSSION

The EcoSEC GPC System with a dual flow refractive index detector was used for analysis of asphalts.

The separation of PMACs by GPC results in three distinctive component peaks. As seen in Figure 1, baseline resolution is obtained between the polymer molecules and the asphaltene and maltene components of the PMACs. The molar mass distributions as obtained by peak position calibration using polystyrene standards results in very distinctive molar mass ranges for each of the PMAC components, i.e., polymer molecule, asphaltenes and maltenes. The molar mass of the polymer molecule ranges from 1.9×10^4 to 5.5×10^6 g/mol, while the molar mass of the asphaltenes and maltenes ranges from 3.0×10^3 to 1.9×10^4 g/mol and 200 to 3.0×10^3 g/mol, respectively.

The final properties of PMACs can vary based on the chemistry and architecture of the polymer molecule added as well as the source of the polymers. Three different sources provided samples of SBS to use as the polymer modifier in PMACs. Figure 2 shows that the SBS from the three different sources vary in polymeric size. Furthermore the SBS sample from Company B results in a single GPC peak while the SBS samples from Company A and Company F are bimodal. The molar mass of the SBS from Company A is twice as large in molar mass as that from Company B and Company F. The SBS polymer modifier varies between suppliers and thus could result in PMACs with different end-use properties.

The ability to reverse engineer asphalts is important thus a method to determine the amount of polymer in a PMAC is essential. To estimate the accuracy and feasibility of using GPC for the analysis of the percentage of polymer in an asphalt mixture compared to the asphaltenes and maltenes, different known amounts of SBS polymer from Company A were mixed with asphaltenes and maltenes and then analyzed via GPC to prove that the chromatogram accurately reflects the change in concentration.

GPC ELUTION PROFILE AND MOLAR MASS AVERAGES OF SBS POLYMER FROM THREE DIFFERENT SUPPLIERS

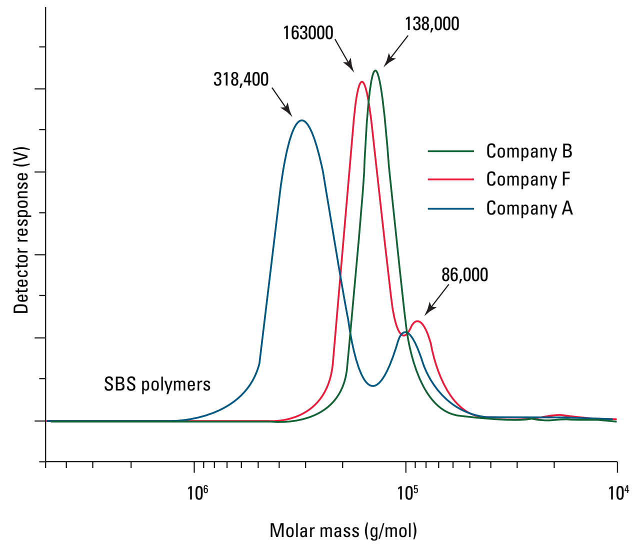

Figure 2

GPC ELUTION PROFILE AND MOLAR MASS AVERAGES OF PMAC COMPONENTS

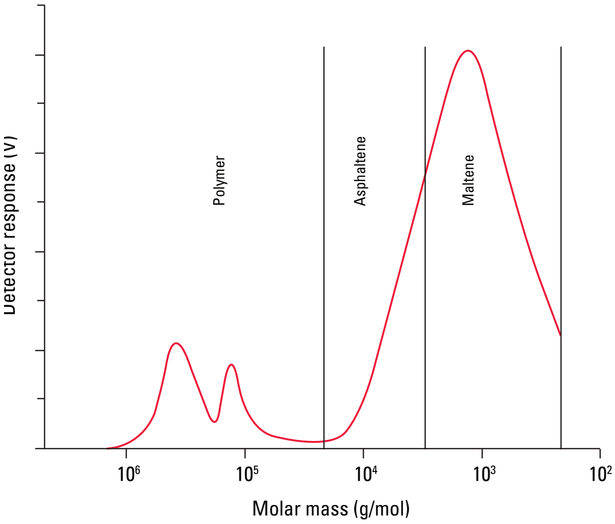

Figure 1

GPC ELUTION PROFILE AND MOLAR MASS AVERAGES OF ASPHALTS WITH DIFFERENT CONCENTRATIONS OF SBS POLYMER FROM COMPANY A

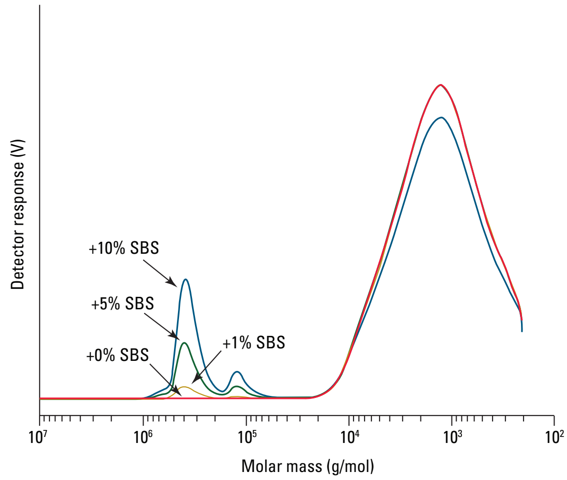

Figure 3

RELATIVE CONCENTRATIONS OF COMPONENTS IN SPIKED SBS ASPHALT MIXTURES

	1000-300K %	300-45K %	45-19K %	Total poymer (%)	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	16.17	78.47
ASPHALT+ 10% SBS	7.77	2.46	0.28	10.51	15.87	73.61

Table 1

The GPC chromatogram for each amount of SBS polymer can be seen in Figure 3 and the corresponding relative component concentrations is given in Table 1. The total percentage of SBS polymer calculated via GPC compares well to the amount of SBS polymer used in each sample.

CONCLUSIONS

The EcoSEC GPC System with a dual flow RI detector was successfully used to separate the three species of PMACs, asphaltenes, maltenes and polymer molecules from one another and to characterize the molar mass averages based on polystyrene standards. GPC analysis of asphalts results in a chromatogram with near baseline resolution between the polymer molecule and the asphaltenes and maltenes. The GPC elution profiles were used to compare SBS polymer from three different suppliers. The SBS from each supplier varied in elution profile, modality, and molar mass. Finally GPC was successfully used as a method for correlating relative concentration values of polymer molecule in asphalts. The use of GPC for the characterization of asphalts and PMACs proves to be a very versatile method.