LOUISIANA TRANSPORTATION RESEARCH CENTER

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Chemical Characterization of Asphalts Related to their Performance

INTRODUCTION

Using recycled asphalt pavements (RAP) and recycled asphalt shingles (RAS) blended with virgin binder for new road pavements is an environmentally friendly way to recycle the used asphalt. In this project, researchers studied a correlation between the molecular structure of asphalt binders of conventional hot mix asphalt mixtures (HMA) containing recycled asphalts (RAS and /or RAP) and/or recycling agents and their cracking potential. The molecular size and structure of asphalt components undergo large changes during its exposure to environmental factors, which affects its physical properties. Gel permeation chromatography (GPC) was used to study the molecular size distribution and Fourier transform infrared spectroscopy (FTIR) was used to study the extent of oxidation (aging) changes in the asphalt binders. The cracking potential of 15 asphalt mixtures was evaluated using the Semi Circular Bend Test (SCB) test procedure.

OBJECTIVE

The objective of this work was to study the effect of adding RAP, RAS and/or, in some cases, recycling agents along with virgin asphalt in HMA mixtures. The contribution of the asphalt component of RAP and RAS additives to the binder properties was evaluated using deconvoluted GPC chromatograms, FTIR, and the SCB test procedure.

SCOPE

Fifteen asphalt mixtures with 12.5-mm nominal maximum aggregate size (NMAS) was evaluated in this study. RAP, Post-consumer waste shingles (RAS-P), and manufacturer waste shingles (RAS-M) were considered in this study. Three types of recycling agents (Hydrogreen, Cyclogen-L, and asphalt flux) were used. A soft binder PG 52-28 and re-refined engine oil bottoms (REOB) were also included in the study. GPC was used to study the molecular size distribution of extracted binders. Deconvolution of the GPC chromatograms allowed detailed analysis of the asphaltene component. A catalog containing data from over 200 GPC deconvoluted chromatograms samples analyzed at DOTD, which were acquired from different companies in Louisiana, was compiled. The amount of and molecular size of the asphaltenes is correlated with the age hardening of asphalt materials. The impact of recycling agents on the asphaltene molecular weight distribution was studied. The extent of aging was confirmed by the carbonyl oxygen content identified from infrared spectroscopic measurements of extracted binders. These data were correlated to the cracking potential of the mixtures to understand the effect of using RAP and/or RAS in HMA mixtures. Recycled samples (RAP and RAS) were tested using GC/MS to ascertain the polycyclic aromatic hydrocarbon content.

METHODOLOGY

A GPC analysis was conducted on binder samples extracted under a nitrogen atmosphere from mixes using hot toluene. The extracted binder samples were recovered from the toluene solution by evaporation and vacuum drying. The neat asphalts were dissolved in tetrahydrofuran (THF) to a concentration of 0.5%. Alternatively, the asphalts from mixtures were extracted with THF in closed

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vials at room temperature (by shaking), left overnight for decantation, and filtered using 0.45-micron Teflon filters. All samples were prepared the previous day and filtered on the day of analysis. GPC was performed using a high-performance system equipped with a differential refractive index detector (RI) and UV detector. A set of four microstyragel columns of pore sizes 200 Å, 75 Å (2 columns), and 30 Å was used for the analysis and THF at a flow rate of 0.35 mL/min. was used to elute the sample. The chromatograms were base line corrected and peak edited using the GPC software and the molecular weight distribution (MWD) curves were generated using a calibration curve obtained using polystyrene standards. The MWD of each sample was divided into three regions of molecular weights, i.e., molecules having size greater than 19,000, molecules having size between 19,000 and 3000, and molecules with size less than 3000 Daltons. The first region can be considered as high molecular weight polymer and highly associated asphaltenes, the second region as asphaltenes, and the third region as maltenes. Determination of the MW of individual species was performed by deconvolution of GPC curves in individual (albeit overlapping) Gaussian peaks giving both the mean MW and their per cent contribution in the same MW range (of 100% integration curve).

During the asphalt mixture design process, the optimum asphalt cement content was determined by varying the virgin binder content while utilizing the same composite aggregate blend until volumetric and densification criteria are met. With the optimum percentage binder content of the mixture and the percentage of virgin binder utilized being known, the actual %RAP and/or %RAS binder contribution in the total binder can be calculated for each mixture. In addition, the actual recycle asphalt availability binder factor, the % RAP and/or %RAS in the binder, and the recycle binder ratio (RBR) can be determined. The RBR is defined as the actual %RAP and/or %RAS binder contribution divided by the design optimum asphalt cement content. For economic benefits, it is important to increase the RBR. Recycling agents were employed to increase the RBR for mixtures containing RAP and/or RAS. At the dosage rate for the RAs selected, all available recycled asphalt binder was utilized and the asphalt mixtures met the volumetric and densification criteria.

To evaluate performance, physical and rheological tests were determined on asphalt binders and hot mix asphalt mixtures (HMA) in a separate LTRC project. In this LTRC project, in addition to asphalt cement rheology characterization, HMA mixture performance and characterization tests were conducted to define permanent deformation (stability), low temperature thermal cracking, and the fatigue life (durability) of HMA mixtures. The presence of RAS impacts the intermediate temperature binder properties that can be characterized using a Semi-Circular Bend (SCB) test to determine the critical strain energy (J_c).

CONCLUSIONS

A comprehensive laboratory evaluation of the composition of asphalt mixtures containing RAP and/or RAS, with and without rejuvenating agents, was conducted. Laboratory testing evaluated molecular composition using SARA, GPC, and intermediate temperature fracture resistance of laboratory produced mixtures using the SCB test. Deconvoluted GPC data allows the identification of associated asphaltene fractions in the aged asphalt binder extracted from RAP, RAS-M, and RAS-P. The concentration of RAS asphaltenes exceeds 40 wt. % of which 25 wt. % are highly aggregated with apparent molecular weights approaching 100K. High concentrations of HMW asphaltenes decrease the fracture resistance of the asphalt mixtures. Mixtures with a high content of asphalt cement species with MW > 20K Daltons (asphaltenes) are relatively brittle. Poor intermediate temperature performance was predicted by J_c values of less than 0.5 kJ/m². Both RAS-M and RAS-P are much more highly oxidized than RAP as indicated by FTIR spectroscopy.

High molecular weight associated asphaltenes are not significantly dissociated by adding rejuvenators. The use of rejuvenators negatively impacted intermediate temperature performance for the mixtures evaluated in this study. The extent of asphalt extraction from RAS increased with the addition of rejuvenators and generally adversely affected the mixtures fracture resistance at intermediate temperature. This may be explained by the additional RAS binder dispersed in the mixture.

The asphaltene component from the SARA analysis was considerably smaller than the asphaltenes determined from deconvoluted GPC chromatograms. The SARA asphaltenes analysis by precipitation did not capture the total amount of associated asphaltenes in the binder as measured by GPC. Some associated asphaltenes may remain in the resin fraction, which is not captured by SARA analysis in the method employed.

AC mixtures containing block copolymeric species with MW > 70K can accommodate 5% RAS and retain satisfactory J_c's of at least 0.5 kJ/m². The residual polymers in RAP may promote compatibility of 5% RAS in mixtures containing virgin asphalt binder and 15% RAP.